We thank the reviewers for their valuable input on the manuscript, and we thank Dr. Hanisco for serving as editor and overseeing the review process. The response to each reviewer comment (red text) is provided below (blue text). Following each response, revisions to manuscript text are indicated in highlighted black text.

**Reviewer #1**

1. The main issue I find with this work is that it completely missed the opportunity to demonstrate the effectiveness of this newly proposed technique with actual measurements of NO and N2O. This seems particularly egregious given the moderate range of NO modeled here (figure 1) that is not difficult to measure directly. Was a NO instrument not available when this work was conceived? Wasn’t producing and maintaining a predictable amount of NO the objective here? Why not show that you achieved this with observations, in addition to model?

**Response.** In an early stage of method development, we conducted a set of experiments where NO and NO\(_2\) were measured following N\(_2\)O (0-3\%), O\(_3\) (1 ppm) and H\(_2\)O (0.07 – 1\%) addition to the reactor. The measurements and their interpretation are not straightforward and are of limited use above [O\(_3\)] ~ 1 ppm, for reasons that are discussed below. However we agree that conveying this information in the manuscript would be useful, and would help to motivate the use of the photochemical model to explore a wider range of operating conditions.

We will add a new Section 3.1 describing the measured NO and NO\(_2\) mixing ratios and comparison with photochemical model outputs. Two accompanying figures, Figure 1 and Figure 2 (below), will be added to the revised manuscript. Subsequent subsections and figures will be renumbered accordingly.

**Revision to Section 2.1.** Changes below incorporate earlier test conditions.

“O\(_3\) (∼1-5 ppm) was generated outside the flow reactor by O\(_2\) irradiation at 185 nm using a mercury lamp. O(\(^{1}\)D) was produced by photolysis of O\(_3\) at 254 nm inside the reactor using two or four mercury lamps”

**Revision to Section 2.2.**

“2.2 NO\(_x\) and chemical ionization mass spectrometer (CIMS) measurements

In one set of experiments, [NO] and [NO\(_2\)] were measured downstream of the reactor with a Thermo Scientific Model 42i chemiluminescent analyzer and an Aerodyne Cavity Attenuated Phase Shift (CAPS) NO\(_2\) analyzer, which measures NO\(_2\) absorption at λ = 450 nm (Kebabian et al., 2008). During these experiments, the following operating conditions were used: I\(_{254}\) = 4\(\times\)10\(^{15}\) ph cm\(^{-2}\) sec\(^{-1}\), [O\(_3\)] = 1
ppm, \([\text{H}_2\text{O}] = 0.07\%\) and 1\%, \([\text{N}_2\text{O}] = 0\) to 3\%. These conditions assess a subset of the attainable operating conditions for comparison with outputs of the photochemical model described in Section 2.3.

The measured NO\textsubscript{2} mixing ratio was decreased by 10 ppb due to absorption by 1 ppm O\textsubscript{3} at 450 nm in the absence of NO\textsubscript{2}. The measured NO mixing ratio was scaled by a factor of 3.2 for depletion downstream of the reactor due to 1.2 sec reaction time with 1 ppm O\textsubscript{3} in the sample line, assuming \(k_{\text{NO} + \text{O}_3} = 1.8 \times 10^{-14}\) cm\(^3\) molec\(^{-1}\) sec\(^{-1}\) and pseudo-first order conditions (Atkinson et al., 2004). Additional NO depletion inside the Thermo analyzer (~47\% at 1 ppm O\textsubscript{3}) was accounted for in a separate experiment where known mixing ratios of NO (50 ppb) and O\textsubscript{3} (0 to 6.9 ppm) were added at the inlet of the instrument (Fig. S1). Because the combined NO depletion in the sample line and the NO analyzer is significantly higher at higher \([\text{O}_3]\) (e.g. ~90\% at \([\text{O}_3] = 2\) ppm and ~99.6\% at \([\text{O}_3] = 5\) ppm), accurate experimental characterization of \([\text{NO}]\) is more difficult above \([\text{O}_3] \sim 1\) ppm.

In another set of experiments, mass spectra of isoprene and \(\alpha\)-pinene gas-phase oxidation products were obtained with an Aerodyne high-resolution time-of-flight mass spectrometer (Bertram et al., 2011)."

Revisions to Section 3.

3.1. Comparison of measured and modeled [NO] and [NO\textsubscript{2}] values following O(\textsuperscript{1}D) + N\textsubscript{2}O and NO + O\textsubscript{3} reactions

Figure 1 compares modeled and measured NO mixing ratios obtained following 80 sec residence time in the reactor at the operating conditions described in Sect. 2.2. The corresponding integrated OH exposures are approximately \(2.6 \times 10^{11}\) and \(2.4 \times 10^{12}\) molec cm\(^{-3}\) sec, respectively, in the absence of added N\textsubscript{2}O. Symbols are colored by \([\text{N}_2\text{O}]\) which ranged from 0 to 3\%. Measured [NO] ranged from 0 to 10.4 ppb and increased with increasing \([\text{N}_2\text{O}]\), as expected, at both \([\text{H}_2\text{O}] = 0.07\%\) and 1\%. The mean ratio of modelled-measured [NO] was 0.94 ± 0.19 at \([\text{H}_2\text{O}] = 0.07\%) and 3.85 ± 2.33 at \([\text{H}_2\text{O}] = 1\%).
Figure 1. Scatter plot comparing measured and modeled [NO] at 80 sec residence time in the PAM oxidation flow reactor, $I_{254} = 4 \times 10^{15}$ ph cm$^{-2}$ sec$^{-1}$, $[O_3] = 1$ ppm, $[H_2O] = 0.07\%$ and $1\%$, $[N_2O] = 0$ to $3\%$. Symbols are colored by $[N_2O]$, with 1:2, 1:1 and 2:1 lines shown for reference. Error bars represent ±60% uncertainty in model outputs (Peng et al., 2015) and ±40% precision in replicate [NO] measurements at fixed $[N_2O]$.

Figure 2. Scatter plot comparing measured and modeled $[NO_2]$ at 80 sec residence time in the PAM oxidation flow reactor, $I_{254} = 4 \times 10^{15}$ ph cm$^{-2}$ sec$^{-1}$, $[O_3] = 1$ ppm, $[H_2O] = 0.07\%$ and $1\%$, $[N_2O] = 0$ to $3\%$. Error bars represent ±60% uncertainty in model outputs (Peng et al., 2015) and ±20% precision in replicate $[NO_2]$ measurements at fixed $[N_2O]$.
NO₂, which is formed by the NO + O₃ reaction, is more straightforward to measure under these conditions because NO₂ reacts approximately 500 times slower than NO with O₃. Thus, a comparison of modeled and measured [NO₂] values provides additional method evaluation with less uncertainty than [NO] measurements. Figure 2 compares corresponding modeled and measured NO₂ mixing ratios obtained during the same experiments described in Figure 1. As expected, [NO₂] increased with increasing [N₂O] because of faster NO + O₃ reaction rate from increasing [NO]. At [H₂O] = 0.07%, measured [NO₂] ranged from 0 to 291 ppb, whereas at [H₂O] = 1%, measured [NO₂] ranged from 0 to 59 ppb. [NO₂] was lower in the latter case because additional OH was formed from O(^1D) + H₂O reactions (Section 2.1), which increased the rate of the OH + NO₂ reaction. The mean ratio of modelled-measured [NO₂] was 0.72 ± 0.39 at [H₂O] = 0.07% and 1.05 ± 0.50 at [H₂O] = 1%. These results, combined with results shown in Figure 1, suggest that an uncharacterized H₂O- or HNO₃-related artifact negatively biased the measured [NO] values at [H₂O] = 1%, and that the photochemical model described in Section 2.3 may be used to evaluate a wider range of reactor operating conditions.

Revision to Supplement. We will add a new Figure S1 (below) to the revised manuscript supplement. Subsequent figures in the Supplement will be renumbered accordingly.

Figure S1. NO depletion inside the NO analyzer due to reaction of 50 ppb initial NO (NO) with O₃. NO was introduced from a calibration cylinder, and O₃ was introduced from the output of the PAM reactor.
**Revision to References.** The following citations will be added.


2. Moreover, measurement of N2O, specifically, the decrease in N2O mixing ratio with increasing radiation intensity would have been helpful to ensure that N2O reaction and photolysis were indeed the reason for the observed changes in CIMS spectra. These two measurements of NO and N2O would have been more convincing than the results from the CIMS, which I find less than convincing, if not, altogether unnecessary.

**Response.** This suggestion is very difficult to implement, with minimal added benefit compared to the CIMS spectra and the [NO] measurements described above. First, please note N2O photolysis is negligible at 254 nm: the main loss pathway under the conditions used in these measurements is N2O + O(^1D). Second, measuring the decrease in [N2O] due to reaction with O(^1D) requires a nearly unattainable level of precision. For example, at 80 sec residence time in the reactor, assuming inputs of [N2O] = 1000 ppb, [H2O] = 1%, and [O3] = 5 ppm, the modeled [N2O] at the exit of the reactor is [N2O] = 999.96 ppb, corresponding to Δ[N2O] = -0.04 ppb or a necessary precision of 0.04/1000 = 0.004%.

**Revision.** We do not think manuscript revisions are necessary in response to this comment.

3. The level of O3 (500 ppb to 50 ppm) required to generate enough O(1D) is still much too high to simulate anything that resembles atmospherically realistic conditions. Limitations are two-fold that I can think of: (1) Given ppm levels of O3, oxidation by ozonolysis can compete with OH oxidation making systematic study of one oxidation pathway versus the other difficult.

**Response.** This is a common misconception. It is true that for some species, and/or non-judicious operating conditions, ozonolysis is too fast to allow the systematic study of OH oxidation difficult. Otherwise, in many cases oxidation by OH remains the dominant loss pathway. We refer the reviewer to the detailed
discussion of this issue in Peng et al. (2016), including the following discussion from Section 3.1.5 of Peng et al. (2016) that is quoted below:

“Among the literature OFR studies, the field studies employing OFRs in urban and forested areas all operated under O$_{3\exp}$/OH$_{\exp}$ values 100 times lower than in the atmosphere. In these field studies reaction of almost all VOCs with O$_3$ can be neglected, except for the most reactive biogenics with O$_3$, e.g., α-terpinene and β-caryophyllene. The source study in an urban tunnel of Tkacik et al. (2014) operated under similar conditions. Some laboratory studies using OFR254 (Kang et al., 2011; Lambe et al., 2011b) as well as the biomass smoke source study (Ortega et al., 2013) operated at O$_{3\exp}$/OH$_{\exp}$ close to tropospheric values, because the injected O$_3$ plays a key role for OFR254 studies and the biomass smoke experiments were conducted at high OHR$_{ext}$.”

We will modify Figures S4d, S5d and S6e in the Supplement to indicate the relative roles of OH, O$_3$ and NO$_3$ for oxidation of isoprene or α-pinene under the experimental conditions that are used. In these figures, the fraction loss of VOC to each oxidant is determined from the integrated OH, O$_3$ and NO$_3$ exposure (calculated using the photochemical model described in Sect. 2.3) and corresponding published OH, O$_3$ and NO$_3$ rate constants. This axis replaces the “OH:NO3” axis shown previously in Figs. S4d, S5d and S6e. As an example, the revised Figure S4 is shown below.

**Revision to Section 2.1.** “In most cases, oxidation of VOCs by O$_3$ is slower than oxidation by OH radical, even with parts per million levels of O$_3$ present (e.g. Peng et al., 2016). NO$_3$ radicals, which are produced as a byproduct of NO$_2$ + O$_3$ or HNO$_3$ + OH reactions, can potentially convolute interpretation of results if the relative oxidation rates of isoprene/α-pinene by OH and NO$_3$ are comparable....”

**Revision to Figure S4** (revised Figures S5-S6 similar format):
4. (2) NO to NO2 ratio also deviates from ambient, such that oxidation by NO3 radical becomes non-negligible (along with production of HNO3, peroxacyl nitrates, etc.). This, the authors note could be as high as 40% of the total oxidation by OH, O3 and NO3 combined. Perhaps the BVOC products from OH vs O3 vs NO3 can be separated using CIMS data, but the presence of different RO2 isomers resulting from each oxidant that may react with one another (RO2+RO2) may mean this simple attribution may not be possible, particularly if the products possess different functional group but same molecular composition.

Response: (1) It is possible to operate under conditions where NO:NO2 is close to ambient ratios using this method. The new figures generated in response to Comment #1 raised by this reviewer should clarify this point: for example, NO2:NO ranges from 4 to 23 over the range of conditions examined in (new) Figures 1 and 2.
(2) Please refer to our response to Comment #7 below, where we discuss in more detail the expected ion signals for acylperoxy nitrates formed from RO₂ + NO₂ reactions and organic nitrate production initiated by VOC + NO₃ reactions.

(3) It is possible to establish conditions where reaction rates of RO₂ + RO₂ are competitive with RO₂ + NO/HO₂ reactions, particularly if high VOC concentrations and/or low oxidant exposures are used. If this were occurring, we would expect a dampening in the effect of changing NO:HO₂ on the distribution of oxidation products (given that RO₂ + RO₂ would be the main termination pathway). This is a caveat that we will state in the revised manuscript.

Revision to Section 2. “Mixing ratios of the gas-phase precursors entering the reactor were 36 ppb for isoprene (diluted from 1000 ppm in N₂, Matheson) and 15 ppb for α-pinene (diluted from 150 ppm in N₂, Matheson). These mixing ratios are a factor of 3 to 10 lower than mixing ratios that are typically required to induce homogenous nucleation of condensable oxidation products in related oxidation flow reactor studies (Lambe et al., 2011b). Minimizing precursor mixing ratios also decreases the rate of RO₂ self-reactions relative to RO₂ + HO₂ and RO₂ + NO reactions. This is a goal for most laboratory experiments that is not specific to the method proposed here. However, this goal takes on added importance when RO₂ can be formed via OH, O₃ and/or NO₃ oxidation using this method (e.g. Section 2.1).”

5. The ppm O₃ levels used here also seem at odds with statements in the abstract and elsewhere in the manuscript that seem to suggest that ppm levels of O₃ are bad (lines 1-5), and that this proposed technique doesn’t require ppm O₃ levels.

Response. We agree that as written this section of the manuscript appears self-contradictory. To clarify our intended message, we revised the text as follows:

Revision to Introduction: “A limitation of flow reactors is the need to use parts-per-million levels of O₃, hindering the possibility to efficiently simulate NOₓ-dependent SOA formation pathways. [...] Here, we present a new method well suited to the characterization of NOₓ-dependent SOA formation pathways in oxidation flow reactors. By utilizing O(¹D) radicals that are generated from O₃ photolysis, we add N₂O to generate NO via the reaction O(¹D) + N₂O → 2NO with no additional method modifications.”

6. In any case, have the authors attempted to run the chamber without O₃? What is the highest level of NO achieved by percent levels of N₂O due to direct photolysis? Given that most suburban+rural+remote regions experience highest NO levels less than 0.5 ppb, perhaps just N₂O and
ambient level of O3 would suffice? This approach may not be suitable for flow reactors, but it may be for the more traditional atmospheric simulation chamber studies.

**Response.** It is not possible to run the chamber without O3, because N2O does not photolyze at 254 nm. The only source of O(1D) at 254 nm is O3 photolysis. Even if 185 nm radiation were added, O3 would still be produced via O2 photolysis.

At 30 ppb O3, 1% N2O, 1% H2O, and I_{254} = 3.2*10^{15} ph cm^{-2} s^{-1}, and 36 ppb added isoprene, 80 sec residence time, model outputs are: OH_{exp} = 5*10^{9} molec cm^{-3} sec (1-2 hr of atmospheric OH oxidation), [NO] = 0.24 ppb. As the reviewer implies, this may be suitable for some studies. However, we note that the relatively high 254 nm actinic flux that is required, combined with the relatively low OH exposure that is generated, significantly increases the potential importance of unwanted photolysis (e.g. Peng et al., 2016).

**Revision.** Because the primary intended application of the method is for use in flow reactors, we do not think manuscript revisions are necessary in response to this comment.

7. The CIMS data show that, yes, as you increase NO, the level of organic nitrates increase, and levels of most organics without a nitrate decreases. This is not surprising. What is missing is that this method of NO generation by N2O in the flow reactor can demonstrate atmospherically relevant chemistry. If CIMS is the instrument of choice, the authors need to compare CIMS spectra of the flow reactor and one that was obtained from ambient atmosphere.

**Response.**

(1) We will add two panels (e) and (f) to Figure 2 in the discussion manuscript. These panels show isoprene-related ions detected in nitrate-CIMS spectra obtained during the SOAS campaign in Centreville, AL under “low-NO” (24 ppt) and “high-NO” (0.53 ppb) ambient conditions. The revised figure and text will facilitate comparison with the same isoprene oxidation products generated in the PAM reactor. Acylperoxy nitrate ion signals formed from RO2 + NO2 reactions (including, but not limited to, C_{2-3}H_{3-5}NO5 signals representing PAN and PPN), as well as possible effects of isoprene + NO3 reactions, will be incorporated and discussed.

(2) We will add one panel (c) to Figure 3. This panel shows α-pinene-related ions detected in nitrate-CIMS spectra obtained during the same “high-NO” conditions plotted in Figure 2f. The revised figure and text will facilitate comparison with the same ion groups detected in α-pinene photoxidation in the
PAM reactor. Acylperoxy nitrate ion signals, as well as possible effects of α-pinene + NO₃ reactions, will be incorporated and discussed.

(3) The x-axis of Figure 2 in the discussions paper ranged from m/Q = 160 to 380 in order to show minor signals at m/z = 351 and 367, (HNO₃NO₃)C₅H₁₀O₂(NO₃)₂ and (HNO₃NO₃)C₅H₁₀O₃(NO₃)₂. We have changed the x-axis scale to m/Q = 160 to 330 to focus on compositional changes in the bulk of the spectra.

(4) In Figure 2 of the discussions paper, we have separated C₄-5H₄-12O₃-8 compounds into C₄H₄,6,8O₄-7 and C₅H₆,8,10,12O₃-8 compounds. This highlights the observation that the C₄:C₅ ratio increases with added NO due to decomposition of alkoxy (RO) radicals formed from RO₂ + NO reactions.

Note: In our response to Reviewer #1 Comment #7, we also address parts of Reviewer #1 Comments #4, #8 and Reviewer #2 Comments #2, #6. The “Figure 3” referenced in the text below refers to a new figure introduced in response to Comment #8.

Revision to Section 2.2. “Mass spectra of isoprene and α-pinene gas-phase oxidation products were obtained with an Aerodyne high-resolution time-of flight mass spectrometer (Bertram et al.,2011) coupled to an atmospheric pressure interface with a nitrate ion chemical ionization source (NO3-HRToF-CIMS, hereafter abbreviated as “NO3-CIMS”) […] The output of the PAM oxidation flow reactor was sampled at 10.5 Lmin⁻¹ through a 2’ length of 0.75” OD stainless steel tubing inserted directly into the rear feedthrough plate of the reactor.

Ambient NO₃⁻ CIMS measurements were conducted during the Southern Oxidant and Aerosol Study (SOAS) at the forest site in Centreville, AL (June 1 - July 15, 2013). At this site, emissions were dominated by local biogenic volatile organic compounds (BVOC) with occasional influence from nearby anthropogenic sources (Hansen et al., 2003). The mixing of biogenic and anthropogenic emissions at the forest site promotes the formation of organic nitrates via oxidation of BVOC in the presence of NOₓ (Lee et al., 2016).”

Revision to Section 3.2. “Ion signals corresponding to isoprene oxidation products shown in Fig. 2 were colored based on classification in ion groups containing 2-5 carbon atoms with zero (C₄H₄,6,8O₄-7 and C₅H₆,8,10,12O₃-8), one (C₂-3H₃,5NO₅ and C₅H₇,9,11NO₆-11), and two (C₅H₁₀N₂O₈-10) nitrogen atoms, where we […] also assume that nitrate functional groups are formed from RO₂ + NO or RO₂ + NO₂ reactions (Sect. 2.1).”

Revision to Section 3.2.2.

“Following addition of N₂O at ~3% mixing ratio, the NO₃-CIMS spectra changed significantly at low and high OH exposures (Figs. 2b, 2d, 4). The signals of C₄-5H₄-12O₃-8 oxidation products decreased, although the C₄H₄,6,8O₄-7 : C₅H₆,8,10,12O₃-8 ratio increased, presumably due to decomposition of alkoxy (RO) radicals formed from reactions of NO with RO₂ radicals containing 5 carbon atoms. The
signals of $\text{C}_2\text{H}_3\text{NO}_5$, $\text{C}_5\text{H}_{7,9,11}\text{NO}_6\text{-}11$, and $\text{C}_5\text{H}_{10}\text{N}_2\text{O}_8\text{-}10$ oxidation products increased.

At low OH exposure, $\text{C}_2\text{H}_3\text{NO}_5$, $\text{C}_5\text{H}_{7,9,11}\text{NO}_3\text{-}8$, and $\text{C}_5\text{H}_{10}\text{N}_2\text{O}_8\text{-}10$ signals constituted 2%, 38%, and 7% of the NO$_3$-CIMS signals, respectively (Fig. 2c), assuming equal CIMS sensitivity and transmission to all detected species. The largest signal in this spectrum was $m/Q = 259$, $\text{C}_5\text{H}_{11}\text{NO}_7$. This compound is a second-generation oxidation product that is formed after two reactions with OH, one RO$_2$ + NO termination reaction and one RO$_2$ + HO$_2$ termination reaction (Fig. 3) (Xiong et al., 2015). A series of additional $\text{C}_5\text{H}_{7,9,11}\text{NO}_6\text{-}11$ ions is also detected. The signal observed at $m/Q = 288$, $\text{C}_5\text{H}_{10}\text{N}_2\text{O}_8\text{-}10$, is a second-generation oxidation product that is formed after two reactions with OH and two RO$_2$ + NO termination reactions (Fig. 3) (Xiong et al., 2015). Other ion signals associated with dinitrate species include $m/Q = 304$, $\text{C}_5\text{H}_{10}\text{N}_2\text{O}_9$, and $m/Q = 320$, $\text{C}_5\text{H}_{10}\text{N}_2\text{O}_{10}$. Related signals were detected at $m/Q = 351$ and 367 (not shown), which we assume represent $(\text{HNO}_3\text{NO}_3)\text{C}_5\text{H}_{10}\text{N}_2\text{O}_8$ and $(\text{HNO}_3\text{NO}_3)\text{C}_5\text{H}_{10}\text{N}_2\text{O}_9$ because we are not aware of other feasible $(\text{NO}_3)^\circ\text{C}_5$ adducts at these mass-to-charge ratios.

At high OH exposure, the same $\text{C}_5\text{H}_{7,9,11}\text{NO}_6\text{-}11$ and $\text{C}_5\text{H}_{10}\text{N}_2\text{O}_8\text{-}10$ species observed at low OH exposure were detected, but at higher concentrations and at higher dinitrate:nitrate. This is presumably due to higher NO:HO$_2$ achieved at higher I$_{254}$ and fixed [N$_2$O] (Figs.1, S1, S4-S5). $\text{C}_2\text{H}_3\text{NO}_5$, $\text{C}_5\text{H}_{7,9,11}\text{NO}_6\text{-}11$, $\text{C}_5\text{H}_{10}\text{N}_2\text{O}_8\text{-}10$, and signals made up 0.3%, 33% and 56%, respectively, of the NO$_3$-CIMS spectrum shown in Fig. 2d, where $\text{C}_5\text{H}_{10}\text{N}_2\text{O}_8$ was the largest signal that was detected.

To demonstrate our ability to mimic atmospheric NO$_x$-dependent photochemistry, Figures 2e and f show $\text{C}_4\text{H}_{4,6,8}\text{O}_4\text{-}7$, $\text{C}_5\text{H}_{6,8,10,12}\text{O}_3\text{-}8$, $\text{C}_2\text{H}_3\text{NO}_5$, $\text{C}_5\text{H}_{7,9,11}\text{NO}_6\text{-}11$, and $\text{C}_5\text{H}_{10}\text{N}_2\text{O}_8\text{-}10$ ion signals detected in NO$_3$-CIMS spectra at the SOAS ground site in Centreville, Alabama, USA. The spectra shown were obtained on 25 Jun 2013 (0730-1100) and 4-5 Jul 2013 (1200 – 0000) which represented periods with sustained “high” and “low” NO mixing ratios of 0.53 ± 0.17 ppb and 0.024 ± 0.025 ppb, respectively, measured at the site. Figures 2a, 2c and 2e indicate that adding N$_2$O to the reactor increases the similarity between the composition of isoprene oxidation products generated at lower photochemical age in the reactor (Figures 2a and 2c) and under “low-NO” ambient conditions (Figure 2e). Likewise, Figures 2b, 2d and 2f indicate that adding N$_2$O to the reactor increases the similarity between the composition of isoprene oxidation products generated at higher photochemical age in the reactor (Figures 2b and d) and at “high-NO” ambient conditions (Figure 2f). We further note that $(\text{HNO}_3\text{NO}_3)\text{C}_5\text{H}_{10}\text{N}_2\text{O}_8\text{-}10$ adducts (not shown) are observed in both laboratory and ambient spectra.

3.2.2.1. Influence of acylperoxy nitrates from RO$_2$ + NO$_2$ reactions
Acylperoxy nitrates (APNs), including peroxy acetyl nitrate (PAN, C$_2$H$_3$NO$_5$) and propionyl peroxy nitrate (PPN, C$_3$H$_5$NO$_5$), are minor components (<2%) of the spectra shown in Figs. 2c-d and 2e-f. APNs are generated from reactions of aldehydic, biogenic VOC oxidation products with OH followed by RO$_2$ + NO$_2$ termination reactions (e.g. LaFranchi et al., 2009). A comparison of Figs. 2c and 2e suggests that yields of PAN and PPN are not enhanced in the reactor compared to atmospheric conditions.

Additional APNs may be generated following the OH oxidation of methacrolein, a first-generation isoprene oxidation product. Methacryloyl peroxy nitrate (MPAN, C$_4$H$_5$NO$_5$) is a second-generation oxidation product formed after one methacrolein + OH reaction and one RO$_2$ + NO$_2$ termination reaction (Orlando et al., 1999). C$_4$-hydroxynitrate-PAN (C$_4$H$_6$N$_2$O$_9$) is a third-generation oxidation product formed through the methacrolein channel after three reactions with OH, two RO$_2$ + NO termination reactions and one RO$_2$ + NO$_2$ termination reaction (Surratt et al., 2010).

Neither C$_4$H$_5$NO$_5$ nor C$_4$H$_6$N$_2$O$_9$ were detected in the laboratory and ambient NO$_3$-CIMS spectra shown in Figs. 2c and 2d. Either these compounds were oxidized or thermally decomposed prior to detection, or their signals were below detection limit. C$_4$H$_7$NO$_5$, which is formed after one methacrolein + OH reaction and one RO$_2$ + NO termination reaction (Surratt et al., 2010), was detected (Fig. 3). Taken together, these observations suggest that yields of APNs are not significantly enhanced in the reactor compared to atmospheric conditions.

3.2.2.2. Influence of isoprene + NO$_3$ reactions

Based on the calculated isoprene + OH and isoprene + NO$_3$ reaction rates (Figs. S4-S5) we assume that isoprene + NO$_3$ reactions have a minor influence on the NO$_3$-CIMS spectra shown in Figs. 2c and 2d. This assumption is further supported by the similarity between laboratory and ambient NO$_3$-CIMS spectra, the latter of which were obtained during the daytime and thus with minimal NO$_3$ exposure (Figs. 2e and f). Specific operating conditions different than those used in this study could increase the relative influence of isoprene + NO$_3$ reactions. In this hypothetical situation, enhanced yields of C$_5$H$_7$NO$_5$, C$_5$H$_8$N$_2$O$_8$ and C$_5$H$_{10}$N$_2$O$_8$ might occur following two reactions with NO$_3$ (Rollins et al., 2009). In addition, C$_5$H$_{10}$N$_2$O$_9$ may be generated from one isoprene + NO$_3$ reaction followed by one RO$_2$ + HO$_2$ termination reaction (Schwantes et al., 2015).

All four of these ions are detected in the spectra shown in Fig. 2, although C$_5$H$_8$N$_2$O$_8$ (not shown in Fig. 2) is present at 0.5% of the intensity of C$_5$H$_{10}$N$_2$O$_8$. If C$_5$H$_8$N$_2$O$_8$ : C$_5$H$_{10}$N$_2$O$_8$ is significantly different under NO$_3$-dominated conditions, this ratio could distinguish the relative rates of isoprene + OH and isoprene + NO$_3$ reactions. Otherwise, it is not clear that the expected product distributions are
significantly different whether isoprene is oxidized by OH or NO$_3$ in the presence of NO$_x$.

**Revisions to Section 3.3.** “Figure 3 shows NO$_3$-CIMS mass spectra of products generated from the oxidation of α-pinene (C10H16). […] C$_{2\text{-}3}$H$_{3,5}$NO$_5$, C$_5$H$_7$NO$_{6\text{-}11}$ […] containing one nitrogen atom […] As was the case with isoprene oxidation products, we assumed nitrogen atoms present in α-pinene oxidation products were associated with nitrate functional groups formed from RO$_2$ + NO or RO$_2$ + NO$_2$ reactions.

**Revisions to Section 3.3.1.** “The signal detected at “low-NOx” conditions […] comprised 5%, 36%, 46%, and 4%, respectively, again assuming equal CIMS sensitivity and transmission to all detected species. The C10 monomers and C19–20 dimers compounds that were observed are often associated with atmospheric new particle formation events […] The remaining ~10% of the signal was classified into C$_{2\text{-}3}$H$_{3,5}$NO$_5$, […] and C$_{10}$H$_{15,17}$NO$_{4\text{-}14}$ ion groups.”

**Revision to Section 3.3.2.** “As was the case with NO$_3$-CIMS spectra of isoprene oxidation products, the addition of N$_2$O to the reactor significantly changed the mass spectrum of α-pinene oxidation products (Figs. 3b and 5). At [N$_2$O] = 3.2%, organic nitrates and dinitrates comprised 62% of the total ion signal (Fig. 3b inset). […] The largest organic nitrate signals in this spectrum were at m/Q = 329, C$_8$H$_{13}$NO$_9$, followed by C$_{10}$H$_{16}$N$_2$O$_9$ (m/Q = 355), C$_{10}$H$_{16}$N$_2$O$_{9\text{-}14}$ signals detected with NO$_3$-CIMS spectra at the Centreville site. The spectra shown here were obtained during the sampling period shown in Fig. 2f and, given the large number of compounds, may include contributions from HOM precursors other than α-pinene. A comparison of Figs. 3a-3c indicates that adding N$_2$O to the reactor increases the similarity between the composition of α-pinene oxidation products generated in the reactor and under “high-NO” ambient conditions, especially in regards to the enhanced C$_5$H$_6$O$_{5\text{-}7}$, C$_5$H$_6$O$_{9\text{-}13}$, C$_{10}$H$_{15,17}$NO$_{9\text{-}14}$, and C$_{10}$H$_{16,18}$N$_2$O$_{6\text{-}13}$ signals are higher in Fig. 3b than in Fig. 3c.

**3.3.2.1. Detection of acylperoxy nitrates (APN) from RO$_2$ + NO$_2$ reactions**

We examined NO$_3$-CIMS spectra of α-pinene oxidation products for the presence of PAN and PPN as components of the C$_{2\text{-}3}$H$_{3,5}$NO$_5$ group. Figs. 3b and 3c indicate that PAN (m/Q = 183, C$_2$H$_3$NO$_5$) and PPN (m/Q = 197, C$_3$H$_5$NO$_5$) are formed at lower yields (<0.4%) than were observed with isoprene (Fig. 2c and 2d). Thus, results suggest that yields of PAN and PPN from reaction of α-pinene-derived-RO$_2$ with NO$_2$ are not enhanced in the reactor compared to atmospheric conditions.
C₉H₁₃NO₆ and C₁₀H₁₅NO₆-8 are APNs generated following OH oxidation of pinonaldehyde, a major first-generation oxidation product of α-pinene, with termination by RO₂ + NO₂ reaction (e.g. Eddingsaas et al., 2012). All four compounds are detected in the reactor and ambient NO₃-CIMS spectra shown in Figs. 3b and 3c, with C₁₀H₁₅NO₆-8 signals among the largest in the spectra. If these signals represent APNs, they appear to be important in both laboratory and atmospheric conditions.

3.3.2.2. Influence of α-pinene + NO₃ reactions

Our calculations suggest that α-pinene + NO₃ reactions may compete with α-pinene + OH reactions at the experimental conditions used to generate the NO₃-CIMS spectrum shown in Fig. 3b. If this were the case, enhanced yields of C₁₀H₁₅NO₆ are anticipated from α-pinene + NO₃ reaction to generate pinonaldehyde, followed by pinonaldehyde + NO₃ reaction and RO₂ + NO₂ termination (Perraud et al., 2010; Nah et al., 2016). Other minor α-pinene + NO₃ products detected with CIMS include C₁₀H₁₅NO₅, C₉H₁₃NO₆, C₁₀H₁₆N₂O₇, and C₁₀H₁₅NO₉ (Nah et al., 2016). We hypothesize that if α-pinene + NO₃ reactions influence the spectrum shown in Fig. 3b, C₁₀H₁₅NO₆ : C₁₀H₁₅NO₈ should be higher in Fig. 3b than in Fig. 3c. Instead, the C₁₀H₁₅NO₆ : C₁₀H₁₅NO₈ ratio was 0.12 in the reactor (Fig. 3b) and 0.28 at the Centreville site (Fig. 3c) during a daytime period with negligible NO₃ influence.

Dinitrates (C₁₀H₁₆,₁₈N₂O₆-1₃) shown in Fig. 3b may originate from two α-pinene + OH reactions followed by two RO₂ + NO terminations, or one α-pinene + NO₃ reaction followed by one RO₂ + NO termination. Given comparable OH and NO₃ reaction rates under these conditions (Fig. S6e), we hypothesize that the majority of dinitrate signals should originate from α-pinene + NO₃ reactions if their yields are not oxidant-dependent. If this is the case, C₁₀H₁₆,₁₈N₂O₆-1₃ : C₁₀H₁₅,₁₇NO₄-1₄ should be larger in Fig. 3b than in Fig. 3c. However, C₁₀H₁₆,₁₈N₂O₆-1₃ : C₁₀H₁₅,₁₇NO₄-1₄ was 0.23 in the spectrum shown in Fig. 3b and 0.61 in the spectrum shown in Fig. 3c.

Thus, while the calculated α-pinene + NO₃ oxidation rate is significant (Fig. S6e), it is not clear that α-pinene + NO₃ oxidation products significantly affect the spectrum shown in Fig. 3b. This may be due to significantly lower organic nitrate yields from α-pinene + NO₃ than from α-pinene + OH reactions in the presence of NO (Fry et al., 2014; Rindelaub et al., 2015).

Revisions to Figures 2 and 3.
Figure 2. NO2-CIMS mass spectra of isoprene oxidation products generated at [H2O] = 1%, [O3] = 5 ppm, mean residence time = 80 sec: (a) I254 = 6.4×10^{13} ph cm^{-2} sec^{-1}, [N2O] = 0%; (b) I254 = 3.2×10^{15} ph cm^{-2} sec^{-1}, [N2O] = 0%; (c) I254 = 6.4×10^{13} ph cm^{-2} sec^{-1}, [N2O] = 3.2%; (d) I254 = 3.2×10^{15} ph cm^{-2} sec^{-1}, [N2O] = 2.9%; (e) and (f) C4H4,6,8,10,12O4-7, C5H6,8,10,12O3-8, C2-3H3,5NO5, C5H7,9,11NO6,11, C5H10N2O8,10 ion groups detected at the SOAS ground site in Centreville, Alabama, USA during (e) “low-NO” and (f) “high-NO” conditions (see text for additional details; C2H2NO3, ions removed from SOAS spectra due to larger contributions from α-pinene + OH oxidation products (Fig. 3). “C,” or “O,” indicate number of carbon or oxygen atoms in labeled ions (not including oxygen atoms associated with nitrate functional groups).
Revisions to References. We added the following citations to references:


8. The discussion sections on the types of oxidation products observed are less than convincing, lacking the detailed mechanism discussions typically included in such studies. As such, these sections read more like speculation.
Response. Since the reviewer did not specify specific text that reads as speculative, we assume (s)he is referring to the following text in Sections 3.2.1 and 3.2.2:

**P7, L10-L12:** “The signal at m/Q = 230, C$_5$H$_{12}$O$_6$ […] is likely a second-generation oxidation product that contains two hydroxyl (OH) and two peroxide (OOH) functional groups (Krechmer et al., 2015; St Clair et al., 2016).”

**P7, L15-L16:** “Previously-identified multi-generation isoprene oxidation products such as C$_5$H$_{10}$O$_5$, C$_5$H$_{12}$O$_5$, and C$_5$H$_{10}$O$_6$ (Surratt et al., 2006; Krechmer et al., 2015; Liu et al., 2016; St Clair et al., 2016) were also detected at significant intensity under low-NO$_x$ conditions.”

**P7, L19-L22:** “At high OH exposure, C$_5$H$_{12}$O$_7$ was the second-largest peak in the spectrum. These highly oxygenated isoprene oxidation products are likely also important in SOA formation processes. We note that C$_5$H$_{10}$O$_7$ is a proposed third-generation, tri-hydroperoxycarbonyl product of isoprene + OH in the absence of NO$_x$ (Peeters et al., 2014).”

**P7-P8, L32-L1:** “The largest signal in this spectrum was m/Q = 259, C$_5$H$_{11}$O$_4$NO$_3$. This compound is likely a second-generation oxidation product that contains two hydroxyl functional groups and one nitrate functional group (Xiong et al., 2015; Liu et al., 2016). A series of additional C$_5$H$_{9,11}$O$_3$-8NO$_3$ ions is also detected. The signal observed at m/Q = 288, C$_5$H$_{10}$O$_2$(NO$_3$)$_2$, is likely a second-generation oxidation product that contains two hydroxyl and two nitrate functional groups (Xiong et al., 2015; Liu et al., 2016).”

To address this comment, we will add a new figure summarizing known pathways of the isoprene + OH oxidation mechanism that form the major ions that are detected with NO$_3$-CIMS (Figure 5 below; “Figure 3” in revised text. Additional benefits of this figure are that it will introduce the proposed structures shown in Figure 4 and will illustrate the steps that are necessary to form methacryloyl peroxy acetyl nitrate (MPAN) and C4-hydroxynitrate-PAN from RO$_2$ + NO$_2$ termination pathways (see Comment #2 by Reviewer 2).

**Revision to Section 3.2.** “Figure 2 shows NO$_3$-CIMS mass spectra of products generated from the oxidation of isoprene […] Thus, it is unlikely that OH suppression at “high OH” and “high NO$_x$” significantly affected the NO$_3$-CIMS spectra shown in Fig. 2.

To aid interpretation of results shown in Fig. 2, Fig. 3 summarizes several known isoprene + OH reaction pathways that are terminated by reactions of RO$_2$ with HO$_2$, NO, or NO$_2$. As will be discussed in the following sections, these
pathways yield multigenerational oxidation products with chemical formulas corresponding to several of the major ions that are plotted in Fig. 2.”

Revision to Section 3.2.1. “[...] The signal at m/Q = 230, C_5H_{12}O_6 (NO_3^-) omitted for brevity here and elsewhere), was the largest signal detected at both low and high OH exposures at “low-NOx” conditions. This species is likely a second-generation oxidation product generated from two reactions with OH and two RO_2 + HO_2 termination reactions (Fig. 3) (Krechmer et al., 2015; St Clair et al., 2016) and is typically associated with isoprene SOA formation and growth under “low-NOx” conditions (Liu et al., 2016). [...] Previously-identified multi-generation isoprene oxidation products such as C_5H_{10}O_5, C_5H_{12}O_5, and C_5H_{10}O_6 (Surratt et al., 2006; Krechmer et al., 2015; St Clair et al., 2016) were also detected at significant intensity under low-NOx conditions. These species are formed after two reactions with OH, one RO_2+ HO_2 termination reaction and one RO_2 + RO_2 termination reaction (Fig. 3). [...] At [...] We note that C_5H_{10}O_7 is a proposed third-generation, tri-hydroperoxycarbonyl product formed after one reaction with OH, two hydrogen shifts and one RO_2 + HO_2 termination reaction as shown in Fig. 3 (Peeters et al., 2014).

Revision to Section 3.2.2. Please see our response to Comment #7 raised by this reviewer. In that response, we revised additional text to incorporate changes associated with the response to this comment.
**Revision to Reference.** The following citation will be added:

9. Does the model account for RO2 chemistry? Is there a model output for the various organic molecular compositions observed or at least groups of organics (i.e. Krechmer 2015 ES&T)?

**Response.** Yes, the model does account for simplified RO2 chemistry. We revised the manuscript to indicate this.

**Revision to Section 2.3.** “The model also includes simplified RO2 chemistry, which is incorporated using the reactions listed below. The addition of these reactions constrain the effects of added isoprene or α-pinene (species “X” below) on steady-state [OH], [HO2] and [NO]:

\[
\begin{align*}
\text{OH} + X & \rightarrow \text{RO2} + \text{H}_2\text{O} \\
\text{RO2} + \text{NO} & \rightarrow \text{RO} + \text{NO2} \quad k = 8\times10^{-12} \\
\text{RO2} + \text{HO2} & \rightarrow \text{ROOH} + \text{O2} \quad k = 1.2\times10^{-11} \\
\text{ROOH} + \text{OH} & \rightarrow \text{RO2} + \text{H}_2\text{O} \quad k = 5.3\times10^{-12}\exp(190./T)\times0.6 \\
\text{ROOH} + \text{OH} & \rightarrow \text{R’HO} + \text{OH} + \text{H}_2\text{O} \quad k = 5.3\times10^{-12}\exp(190./T)\times0.4 \\
\text{RO2} + \text{OH} & \rightarrow \text{RO} + \text{O2} \quad k = 2.3\times10^{-10} \\
\text{RO2} + \text{RO2} & \rightarrow \text{ROOR} \quad k = 5\times10^{-12} \\
\text{RO} + \text{NO} & \rightarrow \text{RNO} + \text{HO2} \quad k = 6\times10^{-15} \\
\text{RO2} + \text{NO} + \text{M} & \rightarrow \text{RNO3} + \text{M} \quad k = 0.02k_{\text{ro2_no}} \\
\text{RO} + \text{NO} + \text{M} & \rightarrow \text{RONO} + \text{M} \quad k = 3\times10^{-11} \\
\text{RO} + \text{NO2} + \text{M} & \rightarrow \text{RONO2} + \text{M} \quad k = 3\times10^{-11}
\end{align*}
\]

Calculated OH exposures…”

10. How much of NO:HO2 changes (x-axis; figures 4 and 5) are due to the reaction of NO with HO2? Is RO2 accounted for in the calculation of NO and HO2?

**Response.** RO2 is (crudely) accounted for in the calculation of NO and HO2 (see reply to previous Comment #9). We calculated the relative rates of NO + HO2, NO + RO2 and HO2 + RO2 reactions for an experiment in which 36 ppb isoprene was
added to the reactor. We specified the following model input parameters: mean residence time = 80 sec, $I_{254} = 3.2 \times 10^{15}$ ph cm$^{-2}$ sec, $[O_3] = 5$ ppm, $[H_2O] = 1\%$, and $[N_2O] = 3\%$. The maximum $[RO_2]$ calculated by the model was 2.6 ppb. At this timestep, $[NO] = 5.3$ ppb and $[HO_2] = 1.4$ ppb. Thus,

\begin{align*}
k[RO_2][NO] &= 6.7 \times 10^{10} \text{ molec cm}^{-3} \text{ sec} \\
k[RO_2][HO_2] &= 2.6 \times 10^{10} \text{ molec cm}^{-3} \text{ sec} \\
k[NO][HO_2] &= 3.9 \times 10^{10} \text{ molec cm}^{-3} \text{ sec}
\end{align*}

This calculation implies that the rate of NO + HO$_2$ reactions is comparable to, or greater than, RO$_2$ + NO and RO$_2$ + HO$_2$ reactions.

**Revision to Section 3.4.** “Figures 4 and 5 show normalized signals of the representative groups of isoprene and α-pinene oxidation products as a function of increasing NO:HO$_2$, which may be influenced by NO + HO$_2$, NO + RO$_2$ and HO$_2$ + RO$_2$ reactions in the reactor that are accounted for in the model. For each group of compounds, signals obtained at a specific NO:HO$_2$ were normalized to the maximum observed signal. NO:HO$_2$ is correlated with the relative branching ratios of RO$_2$ + HO$_2$ and RO$_2$ + NO reactions that govern the distribution of oxidation products observed in Figs. 2 and 3.”

11. Figure 2, judging from the y-axes, much higher signal levels are observed at higher $I_{254}$. Is this the result of production of later-generation oxidation products? Or just more complete oxidation? Was the amount of parent BVOC oxidized measured?

**Response**. We refer the reviewer to the following text in the discussions manuscript; to further clarify this point, we revised the text as shown below. We did not measure the amount of parent BVOC that was oxidized.

Section 3.2.1, P7, L13-L15: “Signals in Figs. 2c-d are approximately 10 times higher than in Figs. 2a-b because additional OH exposure produces higher yields of multi-generation oxidation products that are detected with NO3-CIMS.”

**Revision to Section 3.2.1**: “As shown in Figs.S4 and S5, corresponding OH exposures ranged from $(1.7–2.0)\times10^{10}$ (Fig. 2a and 2c; calculated >82% of isoprene reacted) and $(0.52–2.1)\times10^{12}$ molec cm$^{-3}$ sec (Fig. 2b and 2d; calculated ~100% of isoprene reacted), respectively”.

12. Figure 4 is misleading. From what I understand, the CIMS identifies molecular compositions but cannot assign structure/isomerfunctional groups. What is the source of the drawings on top of figure 4? How were they determined?
Response. We revised the Figure 4 caption to indicate that these are suggested structures based on consistency with previous work. Please also see our response to Comment #8 from this reviewer, where we present a mechanistic figure explaining the anticipated reaction pathways to form these compounds. We will also replace “C_wH_xO_y(NO_3)_z” with “C_wH_xN_yO_y+3_z” representation where applicable throughout the manuscript.

Revision to Figure 4 caption. “Normalized signals of C_4-5H_4-12O_3-8, C_5H_{7,9,11}NO_{6-11}, and C_5H_{10}N_2O_{8-10} isoprene oxidation products as a function of modeled NO:HO_2. For each of the species classes, signals were normalized to the maximum signal. Proposed structures for C_5H_{12}O_6, C_5H_{11}NO_7, and C_5H_{10}N_2O_8 signals are shown as representative ions for each species class (St. Clair et al., 2016; Xiong et al., 2015).”

Reviewer #2

1. While the main goal of this paper is an experimental demonstration of proof of concept of oxidation flow reactors with a dominant contribution of the RO2+NO pathway, it failed to provide convincing evidence that the observed N-containing product formation is due to that pathway. The authors have not ruled out peroxynitrate formation (see comment #2) or products from NO3 oxidation. Although the authors tried explaining the trend of N-containing product signals vs. NO:HO_2 in Section 3.4 and Figures 4 and 5, their discussion seemed to start with the assumption that most N-containing products are formed by RO2+NO, i.e. organic nitrates. This assumption needs to be demonstrated. To clearly demonstrate organic nitrate formation through RO2+NO, I suggest conducting additional experiments where short-chain alkanes (e.g. butane) are used as precursor and OH exposure is limited. In these experiments, acyl RO2 formation is limited, NO3 addition is impossible, RO2 autoxidation is unlikely, and CIMS data should be much simpler to analyze and could contain much clearer information pointing to organic nitrate formation.

Response. It is a fair point that the assumption of N-containing products being formed from RO2 + NO reactions could have been justified more rigorously. In attempt to incorporate this comment into our revised manuscript, we made significant revisions (e.g our response to Comments #7 and #8 raised by Reviewer #1). This reviewer’s suggestion to conduct experiments with short-chain alkanes is well taken but in our opinion is not necessary after the aforementioned revisions. Further, we think it is not practical in conjunction with use of NO3-CIMS as the detector which is more sensitive to multifunctional, highly oxidized,
multigenerational oxidation products that are unlikely to be generated in the experimental systems suggested by the reviewer.

Revision. Please see our response to the comments below.

2. This study completely ignored the possibility of peroxynitrate formation in the PAM. Acylperoxynitrates are relatively stable, especially at short residence times such as in the PAM. NO3-CIMS is unable to distinguish organic nitrates from acylperoxynitrates. Showing tentative structure attribution in e.g. Figure 4 without emphasizing the caveats is very misleading. If N-containing products are mostly acylperoxynitrates formed by RO2+NO2, the new method in this paper may not be as useful as claimed. It should be demonstrated that acylperoxynitrates are not dominant products in the experiments shown in this paper.

Response. We examined the NO3-CIMS spectra obtained under laboratory conditions (with added N2O) and ambient conditions (see Comment #7 by Reviewer 1) for the presence of the following acylperoxy nitrates (APNs):

- Peroxy acetyl nitrate (PAN) at m/Q = 183, (NO3-)C2H3NO5
- Peroxy propionyl nitrate (PPN) at m/Q = 197, (NO3-)C3H5NO5

(isoprene only, as proposed by Surratt et al., 2010)
- Methacryloyl peroxy nitrate (MPAN) at m/Q = 209, (NO3-)C4H5NO5
- C4-hydroxynitrate-PAN at m/Q = 288, (NO3-)C4H6N2O9

(α-pinene only, as proposed by Eddingsaas et al., 2012)
- Norpinonaldehyde PAN at m/Q = 293, (NO3-)C9H13NO6
- Pinonaldehyde PAN at m/Q = 307, (NO3-)C10H15NO6
- Unidentified PAN at m/Q = 323, (NO3-)C10H15NO7
- Unidentified PAN at m/Q = 339, (NO3-)C10H15NO8

If the reviewer is aware of other known APNs derived from isoprene or α-pinene, we would be happy to add them to the revised discussion.

Revision. Please see our response to Comment #7 raised by Reviewer #1, where we also incorporated our response to Comment #2 raised by this reviewer. Overall, we conclude:
(1) isoprene-derived APN’s are formed in at most minor yields in the reactor through the methacrolein channel, because neither MPAN or C4-hydroxynitrate-PAN are detected
(2) A subset of the $\alpha$-pinene-derived organic nitrates may represent APNs formed through the pinonaldehyde channel. If that is the case, the measurements imply that these species are important in both laboratory and ambient conditions.

3. This paper claimed that high NO concentrations and a variable NO:HO2 were obtained by the new method. But these quantities were all only calculated by a model. If these quantities are measured, the claims would be much more convincing, especially for a study that is mainly an experimental demonstration of proof of concept. NO is easy to measure and a method for measuring HO2 with CIMS has recently been published (Sanchez et al., 2016).

Response. Please see our response to Comment #1 raised by Reviewer 1.

Revision. We made significant revisions to the text and added 3 new figures in response to Comment #1 raised by Reviewer 1, which is similar to this comment.

4. At the highest UV used in this study ($3.2 \times 10^{15}$ ph cm$^{-2}$ sec at 254 nm), the UV light can be estimated to destroy >90% O3 by the end of a residence time of 80 s. Moreover, NO, HO2, OH etc. can also consume O3. As a result, both OH and NO production, sustained by O3, would be greatly reduced then and the chemistry close to the exit of the reactor would remarkably deviate from the authors’ original design. However, most experiments in this study were conducted at (nearly) the highest UV. The authors should clarify the impact of O3 being largely destroyed on the chemistry in the PAM.

Response. It is true that processes in the reactor consume O3, but the reviewer’s assertion that >90% of O3 is destroyed at $I_{254} = 3.2 \times 10^{15}$ ph cm$^{-2}$ sec$^{-1}$ is not correct. A significant fraction of O($^1D$) formed from O3 photolysis is quenched to O($^3P$) following collisional stabilization with O2 or N2. O($^3P$) then recombines with O2 to regenerate most of the O3 that is photolyzed. For example, at the conditions mentioned above, if $[O_3]_{initial} = 5$ ppm:

$[H_2O] = 0.07\%$, $[N_2O] = 0\%$: $[O_3]_{final} = 4.8$ ppm (4% ozone destruction)
$[H_2O] = 1\%$, $[N_2O] = 0\%$: $[O_3]_{final} = 3.4$ ppm (32% destruction, upper limit to “low-NO” studies presented in this paper)
$[H_2O] = 1\%$, $[N_2O] = 5\%$: $[O_3]_{final} = 1.6$ ppm (68% destruction, upper limit to “high-NO” studies presented in this paper)

The more relevant point is that less O3 is regenerated in the presence of additional O($^1D$) sinks such as H2O and N2O. It is not clear that this significantly changes the main conclusions of this paper.
Revision to Section 2.1. “Using N₂O as the NOₓ precursor has the following advantages over the simple addition of NO to the carrier gas. First, due to continuous production of O(¹D) from O₃ photolysis inside the reactor (along with minor consumption of N₂O), the spatial distribution of NO and NO₂ is more homogenous. Second, attainable steady-state mixing ratios of NO from N₂O + O(¹D) reactions (ppb levels) are orders of magnitude higher than simple NO injection (sub-ppt levels) as inferred from photochemical model simulations described below in Sect. 2.3. Gradients in [O(¹D)] due to its reaction with H₂O and N₂O alter the spatial distribution of Oₓ, HOₓ and NOₓ in the reactor. To first order, gradients in [O(¹D)] should decrease both [HO₂] and [NO] to a similar extent, and therefore the relative rates of RO₂ + HO₂ and RO₂ + NO termination pathways should remain the same.”

5. In the modeling of this study, it is unclear whether the effect of VOCs in affecting the OH concentration (by shortening OH lifetime) has been considered. If it has already been considered, this should be clarified.

Response. Yes, this has been considered. Please see our response to Comment #9 raised by Reviewer 1.

Revision. Please see our response to Comment #9 raised by Reviewer 1.

6. Organic ozonolysis and NO₃ reactions may be important compared to VOC reactions with OH in the PAM. In particular, α-pinene can be consumed by as much as 40% by NO₃ as mentioned in the paper. The authors should rule out interferences due to NO₃ reactions in the observed MS spectra and discuss the importance of organic ozonolysis relative to reactions with OH.

Response. Please see our replies to Comments #3 and #7 by Reviewer #1. In response to Comment #3 by the other reviewer, we modified Figures S4d, S5d and S6e in the Supplement to indicate the relative roles of OH, O₃ and NO₃ for oxidation of isoprene or α-pinene under the experimental conditions that are used. This axis replaced the “OH:NO3” axis shown previously in Figs. S4d, S5d and S6e. In response to Comment #7 by the other reviewer, we also incorporated our response to this comment, where we added subsections discussing potential interferences from isoprene + NO₃ and α-pinene + NO₃ reactions. The revised Figures S4-S6 imply that the rate of ozonolysis reactions is not fast enough to compete with the rates of OH or NO₃ reactions.

7. Page 5, Line 16: this reaction leads to total N in the model being unconserved. It is unclear to me if this reaction plays a major role. If not, it
should be stated for clarity; otherwise, total N-containing species could be significantly underestimated by the model and a correction to this problem would be needed.

**Response.** Thank you for pointing this out. HNO₄, which would be detected at m/Q = 141, (NO₃⁻)HNO₄, is below the NO₃-CIMS detection limit in these measurements; thus, we assume it is does not play a major role.

**Revision to Section 2.3.** We removed R16 from the list of equations.

8. Page 6, Line 15: it is stated that at lower [N₂O], increasing [O₃] increases [NO]. But this is not clear, since both NO production and loss are approximately proportional to [O₃] and change in [O₃] would have little effect. If the authors did observe this, they need to provide more detail and explain its cause better.

**Response.** Thank you for your insight, which helped us catch a mistake in the model that becomes important at conditions using 50 ppm O₃. After rerunning the model with 0.5, 5, and 50 ppm input O₃ and 1% input N₂O, the trends change: the maximum [NO] occurs at 5 ppm input O₃. This is because at 0.5 ppm input O₃, the NO + OH reaction rate is comparable to NO + O₃. At 50 ppm input O₃, the NO + NO₃ reaction rate exceeds the NO + O₃ reaction rate, to the point that operation at such high O₃ is not advisable. Thus, NO production and loss are not always exactly proportional to O₃.

**Revision to Section 3.1 text.** “At lower [N₂O], increasing [O₃] from 0.5 to 5 ppm increases [NO] because greater NO production from higher [O(1D)] offsets greater NO loss from reaction with OH at 0.5 ppm O₃. Increasing [O₃] from 5 to 50 ppm decreases [NO] because greater NO loss from reaction with NO₃ at 50 ppm O₃ offsets greater NO production from higher [O(1D)]."

**Revision to Supplement.** Revised Figure S2 is shown below.
According to Hyttinen et al. (2015), high HNO₃ concentrations can significantly bias the sensitivities of NO₃-CIMS to different highly oxidized compounds. If calibrations for CIMS data were not accordingly performed, CIMS signals may not be considered proportional to concentrations and it is better to not show signal pie charts, which implies the proportionality, and to highlight this caveat in the text.

**Response.** We removed the pie charts from Figures 2 and 3.

**Revision to Section 3.2.** Figure 2 shows NO₃-CIMS mass spectra [...] To examine changes in relative contributions of C₄H₄,₆,₈O₄-7, C₅H₆,₈,₁₀,₁₂O₃-8, C₅H₇,₉,₁₁NO₆-11, and C₅H₁₀N₂O₈-₁₀ ions as a function of added NOₓ, we made two simplifying assumptions: (1) the NO₃-CIMS had the same sensitivity to all species that were detected, and (2) HNO₃ generated in the reactor did not alter the relative selectivity of the CIMS to different classes of oxidation products, which may not be the case (Hyttinen et al., 2015).
Revision to Section 3.3. “Figure 3 shows NO$_3$-CIMS mass spectra of products generated from the oxidation of $\alpha$-pinene ($\text{C}_{10}\text{H}_{16}$). [...] As was the case with isoprene oxidation products, we assumed [...] the NO$_3$-CIMS had the same sensitivity to all species that were detected, and (3) HNO$_3$ generated in the reactor did not alter the relative selectivity of the CIMS to different classes of oxidation products (Hyttilinen et al., 2015).”

Revision to References. Added citation for:


10. Page 1, Line 17: it would be better to use the term “highly oxidized molecules (HOM)” instead of “ELVOC”, as highly oxidized species may not have extremely low volatility (Kurtén et al., 2016).

Revision to Introduction. “Recent atmospheric observations supported by experimental and theoretical studies show that highly oxidized molecules (HOM), together with sulfuric acid, are involved in the initial nucleation steps leading to new particle formation (NPF) (Donahue et al., 2013; Riccobono et al., 2014; Kurtén et al., 2016).

Revision to References: Added citation for:


11. Page 3, Line 16: “condensible” should be “condensable”

Revision to Section 2. “These mixing ratios are a factor of 3 to 10 lower than mixing ratios that are typically required to induce homogenous nucleation of condensable oxidation products in related oxidation flow reactor studies (Lambe et al., 2011b).”

12. Page 5, Line 4: “+M” should be added on both sides of the chemical equation.
Revision to Section 2.3: “NO+OH + M → HONO + M”

13. Page 9, Line 4: a space needed between "into" and "C5H7O6-11NO3"

Revision to Section 3.3.1. This change will be incorporated in the revised manuscript.

References


Controlled nitric oxide production via O(\textsuperscript{1}D)+N\textsubscript{2}O reactions for use in oxidation flow reactor studies

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Abstract.

Oxidation flow reactors that use low-pressure mercury lamps to produce hydroxyl (OH) radicals are an emerging technique for studying the oxidative aging of organic aerosols. Here, ozone (O\textsubscript{3}) is photolyzed at 254 nm to produce O(\textsuperscript{1}D) radicals, which react with water vapor to produce OH. However, the need to use parts-per-million levels of O\textsubscript{3} hinders the ability of oxidation flow reactors to simulate NO\textsubscript{x}-dependent SOA formation pathways. Simple addition of nitric oxide (NO) results in fast conversion of NO\textsubscript{x} (NO + NO\textsubscript{2}) to nitric acid (HNO\textsubscript{3}), making it impossible to sustain NO\textsubscript{x} at levels that are sufficient to compete with hydroperoxy (HO\textsubscript{2}) radicals as a sink for organic peroxy (RO\textsubscript{2}) radicals. We developed a new method that is well suited to the characterization of NO\textsubscript{x}-dependent SOA formation pathways in oxidation flow reactors. NO and NO\textsubscript{2} are produced via the reaction O(\textsuperscript{1}D) + N\textsubscript{2}O \rightarrow 2NO, followed by the reaction NO + O\textsubscript{3} \rightarrow NO\textsubscript{2} + O\textsubscript{2}. Laboratory measurements coupled with photochemical model simulations suggest that O(\textsuperscript{1}D) + N\textsubscript{2}O reactions can be used to systematically vary the relative branching ratio of RO\textsubscript{2} + NO reactions relative to RO\textsubscript{2} + HO\textsubscript{2} and/or RO\textsubscript{2} + RO\textsubscript{2} reactions over a range of conditions relevant to atmospheric SOA formation. We demonstrate proof of concept using high-resolution time-of-flight chemical ionization mass spectrometer (HR-ToF-CIMS) measurements with nitrate (NO\textsubscript{3}\textsuperscript{-}) reagent ion to detect gas-phase oxidation products of isoprene and α-pinene previously observed in NO\textsubscript{x}-influenced environments and in laboratory chamber experiments.

1 Introduction

Recent atmospheric observations supported by experimental and theoretical studies show that highly oxygenated, extremely low-volatility organic compounds (ELVOC) oxidized molecules (HOM), together with sulfuric acid, are involved in the initial
nucleation steps leading to new particle formation (NPF) (Donahue et al., 2013; Riccobono et al., 2014). ELVOC (Donahue et al., 2013; Riccobono et al., 2014; Kurten et al., 2016). HOM form rapidly in the gas phase via auto-oxidation processes (Crounse et al., 2013; Rissanen et al., 2014) and tend to condense irreversibly (Ehn et al., 2014). Following NPF, semivolatile organic compounds (SVOC) with higher vapor pressures condense on newly formed aerosols at rates influenced by their volatility (Donahue et al., 2012), ultimately driving nanoparticle growth towards formation of cloud condensation nuclei (CCN) (Pierce et al., 2012; Riipinen et al., 2012). NPF events may produce as much as 50% of global CCN (Merikanto et al., 2009; Yu and Luo, 2009). However, mechanisms that govern the formation of specific ELVOCs and condensation of SVOCs in various source regions are largely unknown.

The extent to which NPF and growth is influenced by natural and anthropogenic emissions, separately and together, is still unknown. In some locations, biogenic SOA formation is enhanced by anthropogenic carbonaceous aerosol particles, SO$_x$ and/or NO$_x$ (Carlton et al., 2010; Shilling et al., 2013; Xu et al., 2015). At the moment, one can only speculate about some of the possible synergistic or antagonistic chemical mechanisms regulating these processes. For example, anthropogenic emissions can enhance biogenic SOA formation by providing seed particles for condensable biogenic vapors. On the other hand, isoprene can slow down the formation of SOA from other volatile organics, possibly by depleting the local concentration of OH without itself producing significant SOA yields (Pugh et al., 2011). Globally the source strength of anthropogenic SOA is poorly constrained, with an uncertainty of at least a factor of 2 or 3 (Spracklen et al., 2011). Large uncertainties in pre-industrial aerosol emissions and processes further confound our understanding of the direct and indirect effects of anthropogenic aerosol emissions (Carslaw et al., 2014) and the impact of aerosols on climate (Andreae and Gelencsér, 2006).

To date, environmental chamber experiments have generated most of the laboratory SOA yield data used in atmospheric models, especially in simulations of polluted atmospheric conditions with elevated NO$_x$ concentrations. However, NO$_x$-dependent chambers studies are complicated by the need to use multiple OH radical precursors such as hydrogen peroxide (H$_2$O$_2$) and nitrous acid (HONO) or methyl nitrite (CH$_3$ONO) to span the relevant range of NO$_x$ levels (typically, H$_2$O$_2$ for low-NO$_x$ conditions and HONO or CH$_3$ONO for high-NO$_x$ conditions) (Ng et al., 2007). Additionally, chambers have relatively low throughput and are limited to residence times of several hours due to chamber deflation and/or loss of particles and oxidized vapors to the chamber walls (Zhang et al., 2014). This restricts environmental chambers to simulating atmospheric aerosol particle lifetimes and SOA yields only up to 1 or 2 days, therefore limiting the study of formation of highly oxygenated SOA characteristic of aged atmospheric organic aerosol PM (Ng et al., 2010) unless very low VOC precursor concentrations are used (Shilling et al., 2009; Pfaffenberger et al., 2013).

Oxidation flow reactors have recently been developed to study SOA formation and evolution over time scales ranging from hours to multiple days of equivalent atmospheric OH exposure. In these reactors, O$_3$ is photolyzed at 254 nm to produce O($^1$D) radicals, which react with water vapor to produce OH radicals. OH concentrations are typically $10^8$ cm$^{-3}$ or greater. Under these conditions, atmospheric photochemical aging timescales up to $\sim$10 days can be simulated at flow tube residence times of a few minutes or less. Recent experimental studies suggest that flow reactor-generated SOA particles have compositions similar to SOA generated in smog chambers (Bruns et al., 2015; Lambe et al., 2015) and in the atmosphere (Tkacik et al., 2014; Ortega et al., 2016; Palm et al., 2016). Modeling studies suggest that flow reactors can simulate tropospheric oxidation reactions with minimal experimental artifacts (Li et al., 2015; Peng et al., 2015, 2016). A limitation of flow reactors is the need...
to use parts-per-million levels of O$_3$, hindering the possibility to efficiently simulate NO$_x$-dependent SOA formation pathways. Simple addition of NO to flow reactors, while possible (Liu et al., 2015), cannot sustain NO$_x$ mixing ratios at levels that are sufficient to compete with hydroperoxy (HO$_2$) radicals as a sink for organic peroxy (RO$_2$) radicals due to fast conversion of NO$_x$ to nitric acid (HNO$_3$) \textit{via the reactions} $\text{NO} + \text{O}_3 \rightarrow \text{NO}_2$ and $\text{NO}_2 + \text{OH} \rightarrow \text{HNO}_3$. Here, we present a new method well suited to the characterization of NO$_x$-dependent SOA formation pathways in oxidation flow reactors. \textbf{By utilizing} O($^{1}\text{D}$) radicals that are generated from O$_3$ photolysis, we add N$_2$O to generate NO \textit{via the reaction} O($^{1}\text{D}$) + N$_2$O $\rightarrow$ 2NO with no additional method modifications. We validate the concept using high-resolution time-of-flight chemical ionization mass spectrometer measurements (HR-ToF-CIMS) to detect gas-phase oxidation products of isoprene and $\alpha$-pinene that have been observed in NO$_x$-influenced environments and laboratory chamber experiments.

2 Experimental

Experiments were conducted using an Aerodyne Potential Aerosol Mass (PAM) oxidation flow reactor, which is a horizontal 13.3 L aluminum cylindrical chamber (46 cm long $\times$ 22 cm ID) operated in continuous flow mode (Kang et al., 2007; Lambe et al., 2011a). The average residence time was 80 s. The relative humidity (RH) in the reactor was controlled in the range of 3–35 % at 22°C, corresponding to H$_2$O mixing ratios of approximately 0.07 - 1%. The irradiance in the reactor was measured using a photodiode (TOCON-C6, sglux Gmbh). The gas-phase SOA precursors used in these studies include two biogenic compounds (isoprene, $\alpha$-pinene) that were prepared in compressed gas cylinders and introduced to the reactor at controlled rates using a mass-flow controller. Mixing ratios of the gas-phase precursors entering the reactor were 36 ppb for isoprene (diluted from 1000 ppm in N$_2$, Matheson) and 15 ppb for $\alpha$-pinene (diluted from 150 ppm in N$_2$, Matheson). These mixing ratios are a factor of 3 to 10 lower than mixing ratios that are typically required to induce homogenous nucleation of condensible oxidation products in related oxidation flow reactor studies (Lambe et al., 2011b). \textbf{Minimizing precursor mixing ratios also decreases the rate of RO$_2$ self-reactions relative to RO$_2$ + HO$_2$ and RO$_2$ + NO reactions. This is a goal for most laboratory experiments that is not specific to the method proposed here. However, this goal takes on added importance when RO$_2$ can be formed \textit{via} OH, O$_3$ and/or NO$_3$ oxidation using this method as discussed in Section 2.1.}

2.1 OH radical and NO$_x$ generation

OH radicals were produced in the reactor via the reaction $\text{O}(^{1}\text{D}) + \text{H}_2\text{O} \rightarrow 2\text{OH}$, with $\text{O}(^{1}\text{D})$ radicals produced from the reaction $\text{O}_3 + \nu \rightarrow \text{O}_3 + \text{O}(^{1}\text{D})$. O$_3$ ($\sim$5-15 ppm) was generated outside the flow reactor by O$_2$ irradiation at 185 nm using a mercury fluorescent lamp (GPH212T5VH, Light Sources, Inc.). O($^{1}\text{D}$) was produced by photolysis of O$_3$ at 254 nm inside the reactor using two or four mercury fluorescent lamps (GPH436T5L, Light Sources, Inc.). A fluorescent dimming ballast was used to regulate current applied to the lamps. To vary [OH] inside the reactor, I$_{254}$ was varied by changing the dimming voltage applied to the ballast between 1.6 and 10 VDC. At these conditions, I$_{254}$ ranged from approximately $(0.064 - 3.2) \times 10^{15}$ ph cm$^{-2}$ sec. The highest I$_{254}$ value was calculated from the internal surface area of the reactor and the lamp output at maximum
intensity (e.g. 10 VDC) specified by the manufacturer. Lower \( I_{254} \) values were calculated from the measured irradiance at lower dimming voltage relative to the measured irradiance and manufacturer-specified lamp output at 10 VDC.

NO and NO\(_2\) were produced via the reaction \( \text{N}_2\text{O} + \text{O}^{(1)}\text{D} \rightarrow 2\text{NO} \), followed by the reaction \( \text{NO} + \text{O}_3 \rightarrow \text{NO}_2 \). \( \text{N}_2\text{O} \) (99.5\%) was introduced from a compressed gas cylinder at flow rates ranging from 0 to 648 cm\(^3\) min\(^{-1}\), corresponding to mixing ratios of 0\% to 5.6\% at the carrier gas flow rates that were used. Using \( \text{N}_2\text{O} \) as the \( \text{NO}_x \) precursor has the following advantages over the simple addition of NO to the carrier gas. First, due to continuous production of \( \text{O}^{(1)}\text{D} \) from \( \text{O}_3 \) photolysis inside the reactor (along with minor consumption of \( \text{N}_2\text{O} \)), the spatial distribution of NO and NO\(_2\) is more homogenous. Second, attainable steady-state mixing ratios of NO from \( \text{N}_2\text{O} + \text{O}^{(1)}\text{D} \) reactions (ppb levels) are orders of magnitude higher than simple NO injection (sub-ppt levels) as inferred from photochemical model simulations described below in Sect. 2.3. Third, photolysis of \( \text{N}_2\text{O} \) at 185 nm (if used) provides an additional source of \( \text{O}^{(1)}\text{D} \) from the reaction \( \text{N}_2\text{O} + h\nu \rightarrow \text{N}_2 + \text{O}^{(1)}\text{D} \).

We assume background [NO] < 0.05 ppb in the reactor based on separate [NO] measurements and calculate additional NO formed from \( \text{N}_2\text{O} + \text{O}^{(1)}\text{D} \) reactions using the model described in Sect. 2.3. Gradients in [\( \text{O}^{(1)}\text{D} \)] due to its reaction with \( \text{H}_2\text{O} \) and \( \text{N}_2\text{O} \) may alter spatial distributions of \( \text{O}_{x_1} \), \( \text{HO}_x \) and \( \text{NO}_x \) in the reactor. To first order, gradients in [\( \text{O}^{(1)}\text{D} \)] decrease both [\( \text{HO}_2 \)] and [NO] to a similar extent, keeping the relative rates of \( \text{RO}_2 + \text{HO}_2 \) and \( \text{RO}_2 + \text{NO} \) termination pathways the same.

In most cases, oxidation of VOCs by \( \text{O}_3 \) is slower than oxidation by OH radical, even with parts per million levels of \( \text{O}_3 \) present (Peng et al., 2016). \( \text{NO}_3 \) radicals, which are produced as a byproduct of NO\(_2 + \text{O}_3 \) or HNO\(_3 + \text{OH} \) reactions, can potentially convolute interpretation of results if the relative oxidation rates of isoprene/\( \alpha \)-pinene by OH and \( \text{NO}_3 \) are comparable. For results presented in Sects. 3.3 and 3.4, calculated OH, \( \text{O}_3 \) and \( \text{NO}_3 \) exposures combined with published OH, \( \text{O}_3 \) and \( \text{NO}_3 \) rate constants (Atkinson, 1986, 1991; Atkinson, 1986, 1991; Grosjean and Grosjean, 1996) suggest that the relative contribution of \( \text{NO}_3 \) to isoprene and \( \alpha \)-pinene oxidation ranges from approximately 0 to 4\% and 0 to 40\%, respectively, as a function of [\( \text{N}_2\text{O} \)]. Thus, reaction rates of \( \alpha \)-pinene with OH, \( \text{O}_3 \) and \( \text{NO}_3 \) may be comparable under a subset of experimental conditions. Potential implications are discussed in more detail in Sect. 3.4. Sections 3.3.4 and 3.4.4.

### 2.2 Chemical-\( \text{NO}_x \) and chemical ionization mass spectrometer (CIMS) measurements

Mass-In one set of experiments, [NO] and [NO\(_2\)] were measured downstream of the reactor with a Thermo Scientific Model 42i chemiluminescent analyzer and an Aerodyne Cavity Attenuated Phase Shift (CAPS) NO\(_2\) analyzer, which measures NO\(_2\) absorption at \( \lambda = 450 \text{ nm} \) (Kebabian et al., 2008). During these experiments, the following operating conditions were used: \( I_{254} \equiv 4 \times 10^{15} \text{ ph cm}^{-2} \text{ sec}^{-1} \), \( [\text{O}_3] = 1 \text{ ppm} \), \( [\text{H}_2\text{O}] = 0.07\% \text{ and } 1\% \), \( [\text{N}_2\text{O}] = 0 \text{ to } 3\% \). These conditions assess a subset of the attainable operating conditions for comparison with outputs of the photochemical model described in Section 2.3. The measured NO\(_2\) mixing ratio was decreased by 10 ppb due to absorption by 1 ppm \( \text{O}_3 \) at 450 nm in the absence of NO\(_2\). The measured NO mixing ratio was scaled by a factor of 3.2 for depletion downstream of the reactor due to 1.2 sec reaction time with 1 ppm \( \text{O}_3 \) in the sample line, assuming \( k_{\text{NO}}^{\text{NO}} = 1.8 \times 10^{-14} \text{ cm}^3 \text{ molec}^{-1} \text{ sec}^{-1} \) and pseudo-first order conditions (Atkinson et al., 2004). Additional NO depletion inside the chemiluminescent analyzer (\( \sim 47\% \) at 1 ppm \( \text{O}_3 \)) was accounted for in a separate experiment where known mixing ratios of NO (50 ppb) and \( \text{O}_3 \) (0 to 6.9 ppm) were added at the inlet of the
instrument (Fig. S1). Because the combined NO depletion in the sample line and the chemiluminescent analyzer is significantly higher at higher \([O_3]\) (e.g. \(\sim 90\%\) at \([O_3] = 2\) ppm and \(\sim 99.6\%\) at \([O_3] = 5\) ppm), accurate experimental characterization of \([\text{NO}]\) is more difficult above \([O_3] \sim 1\) ppm.

In another set of experiments, mass spectra of isoprene and \(\alpha\)-pinene gas-phase oxidation products were obtained with an Aerodyne high-resolution time-of-flight mass spectrometer (Bertram et al., 2011) coupled to an atmospheric pressure interface with a nitrate ion chemical ionization source (\(\text{NO}_3^-\)-HRToF-CIMS, hereafter abbreviated as “\(\text{NO}_3^-\)-CIMS”) (Eisele and Tanner, 1993; Ehn et al., 2012). Nitrate (\(\text{NO}_3^-\)) and its higher order clusters (e.g. \(\text{HNO}_3\text{NO}_3\)) generated from x-ray ionization of \(\text{HNO}_3\) were used as the reagent due to the selectivity to highly oxidized organic compounds, including species that contribute to SOA formation (Ehn et al., 2014; Krechmer et al., 2015). Isoprene and \(\alpha\)-pinene oxidation products were detected as adducts with \(\text{NO}_3^-\) or \(\text{HNO}_3\text{NO}_3\). CIMS data were analyzed using the Tofware software package (Tofwerk AG, Aerodyne Research, Inc.) implemented in IGOR Pro 6 (Wavemetrics, Inc.). The output of the PAM oxidation flow reactor was sampled at 10.5 L min\(^{-1}\) through a 2’ length of 0.75” OD stainless steel tubing inserted directly into the rear feedthrough plate of the reactor.

Ambient \(\text{NO}_3^-\)-CIMS measurements were conducted during the Southern Oxidant and Aerosol Study (SOAS) at the forest site in Centreville, AL (June 1 - July 15, 2013). At this site, emissions were dominated by local biogenic volatile organic compounds (BVOC) with occasional influence from nearby anthropogenic sources (Hansen et al., 2003). The mixing of biogenic and anthropogenic emissions at the forest site promotes the formation of organic nitrates via oxidation of BVOC in the presence of \(\text{NO}_x\) (Lee et al., 2016).

### 2.3 Photochemical modeling

We used a photochemical model Li et al. (2015); Peng et al. (2015) (Li et al., 2015; Peng et al., 2015) implemented in MATLAB (Mathworks) to calculate concentrations of radical/oxidant species produced in the reactor. Model input parameters included pressure, temperature, \([\text{H}_2\text{O}]\), \([\text{O}_3]\), \([\text{N}_2\text{O}]\), \(I_{254}\), mean residence time, and the input mixing ratios of isoprene and \(\alpha\)-pinene. Differential equations used to describe the radical/oxidant chemistry were integrated at 5 millisecond time steps. The following reactions and associated kinetic rate constants (Sander et al., 2000, 2006) were implemented to describe NO\(_x\) chemistry in the reactor:
\[ \text{N}_2\text{O} + h\nu \rightarrow \text{N}_2 + \text{O}^1\text{D} \quad \text{(R1)} \]
\[ \text{N}_2\text{O} + \text{O}^1\text{D} \rightarrow 2\text{NO} \quad \text{(R2)} \]
\[ \text{N}_2\text{O} + \text{O}^1\text{D} \rightarrow \text{N}_2 + \text{O}_2 \quad \text{(R3)} \]
\[ \text{NO} + \text{OH} \rightarrow \text{HONO} + \text{M} \rightarrow \text{HONO} + \text{M} \quad \text{(R4)} \]
\[ \text{NO} + \text{HO}_2 \rightarrow \text{OH} + \text{NO}_2 \quad \text{(R5)} \]
\[ \text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2 \quad \text{(R6)} \]
\[ \text{NO}_2 + \text{O} \rightarrow \text{NO} + \text{O}_2 \quad \text{(R7)} \]
\[ \text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 + \text{O}_2 \quad \text{(R8)} \]
\[ \text{NO}_3 + \text{O} \rightarrow \text{NO}_2 + \text{O}_2 \quad \text{(R9)} \]
\[ \text{HONO} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{NO}_2 \quad \text{(R10)} \]
\[ \text{NO}_2 + \text{NO}_3 + \text{M} \rightleftharpoons \text{N}_2\text{O}_5 + \text{M} \quad \text{(R11)} \]
\[ \text{NO} + \text{NO}_3 \rightarrow 2\text{NO}_2 + \text{O}_2 \quad \text{(R12)} \]
\[ \text{NO}_2 + \text{OH} + \text{M} \rightarrow \text{HNO}_3 + \text{M} \quad \text{(R13)} \]
\[ \text{NO}_2 + \text{HO}_2 + \text{M} \rightarrow \text{HNO}_4 + \text{M} \quad \text{(R14)} \]
\[ \text{N}_2\text{O}_5 + \text{H}_2\text{O} \rightarrow 2\text{HNO}_3 \quad \text{(R15)} \]
\[ \text{HNO}_4 + \text{OH} \rightarrow \text{products} \quad \text{HNO}_3 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{NO}_3 \quad \text{(R16)} \]
\[ \text{NO}_3 + \text{NO}_3 \rightarrow 2\text{NO}_2 + \text{O}_2 \quad \text{(R17)} \]

The model also includes simplified RO\textsubscript{2} chemistry, which is incorporated using the reactions listed below (IUPAC, 2013). The addition of these reactions constrain the effects of added isoprene or α-pinene (species “X” below) on steady-state [OH]. [HO\textsubscript{2}] and [NO]. Second-generation organic radical products of initial organic radical reactions (“RPHO”, “RPO\textsubscript{2}”, “RPO”) are not reacted further in the model.
\[
\text{OH} + X \rightarrow \text{RO}_2 + \text{H}_2\text{O} \quad \text{(R18)}
\]
\[
\text{RO}_2 + \text{NO} \rightarrow \text{RO} + \text{NO}_2 \quad \text{(R19)}
\]
\[
\text{RO}_2 + \text{HO}_2 \rightarrow \text{ROOH} + \text{O}_2 \quad \text{(R20)}
\]
\[
\text{ROOH} + \text{OH} \rightarrow \text{RO}_2 + \text{H}_2\text{O} \quad \text{(R21)}
\]
\[
5 \text{ ROOH} + \text{OH} \rightarrow \text{RPHO} + \text{OH} + \text{H}_2\text{O} \quad \text{(R22)}
\]
\[
\text{RO}_2 + \text{OH} \rightarrow \text{RPO}_2 + \text{H}_2\text{O} \quad \text{(R23)}
\]
\[
\text{RO}_2 + \text{RO}_2 \rightarrow \text{ROOR} \quad \text{(R24)}
\]
\[
\text{RO} + \text{O}_2 \rightarrow \text{RPO} + \text{HO}_2 \quad \text{(R25)}
\]
\[
\text{RO}_2 + \text{NO} + \text{M} \rightarrow \text{RO}_2\text{NO} + \text{M} \quad \text{(R26)}
\]
\[
10 \text{ RO} + \text{NO} + \text{M} \rightarrow \text{RONO} + \text{M} \quad \text{(R27)}
\]
\[
\text{RO} + \text{NO}_2 + \text{M} \rightarrow \text{RONO}_2 + \text{M} \quad \text{(R28)}
\]

Calculated OH exposures (product of mean OH concentration and residence time) ranged from $1.7 \times 10^{10}$ to $2.1 \times 10^{12}$ molec cm$^{-3}$ sec or approximately 3 hours to 16 days of equivalent atmospheric exposure at $[\text{OH}] = 1.5 \times 10^6$ cm$^{-3}$ (Mao et al., 2009). Steady-state $[\text{NO}]$ and $[\text{HO}_2]$ ranged from 0 to 13.5 ppb and 0.01 to 2.1 ppb, respectively, depending on $[\text{N}_2\text{O}]$, $[\text{H}_2\text{O}]$, $[\text{O}_3]$ and $I_{254}$. We assumed ±25% uncertainty in the calculated OH exposure and ±60% uncertainty in other model outputs (Peng et al., 2015). For ratios of model outputs with independent ±60% uncertainties (e.g. NO:HO$_2$), propagated uncertainties of ±85% were assumed. Addition of N$_2$O at the highest mixing ratios that were used suppressed [OH] because N$_2$O competes with H$_2$O as a sink for O($^1\text{D}$). Potential consequences of OH suppression are discussed where applicable in Sects. 3.3 and 3.4.

3 Results and Discussion

3.1 Comparison of measured and modeled [NO] and [NO$_2$] values following O($^1\text{D}$) + N$_2$O and NO + O$_3$ reactions

Figure 1 compares modeled and measured NO mixing ratios obtained following 80 sec residence time in the reactor at the operating conditions described in Sect.2.2. The corresponding integrated OH exposures are approximately $2.6 \times 10^{11}$ and $2.4 \times 10^{12}$ molec cm$^{-3}$ sec, respectively, in the absence of added N$_2$O. Symbols are colored by [N$_2$O] which ranged from 0 to 3%. Measured [NO] ranged from 0 to 10.4 ppb and increased with increasing [N$_2$O], as expected, at both [H$_2$O] = 0.07% and 1%. The mean ratio of modeled-measured [NO] was $0.94 \pm 0.19$ at [H$_2$O] = 0.07% and $3.85 \pm 2.33$ at [H$_2$O] = 1%.

NO$_2$, which is formed by the NO + O$_3$ reaction, is more straightforward to measure under these conditions because NO$_2$ reacts approximately 500 times slower than NO with O$_3$. Thus, a comparison of modeled and measured [NO$_2$] provides additional method evaluation with less uncertainty than [NO] measurements. Figure 2 compares corresponding modeled and measured NO$_2$ mixing ratios obtained during the same experiments described in Figure 1. As expected, [NO$_2$] increased
with increasing \([N_2O]\) because of faster \(NO + O_3\) reaction rate from increasing \([NO]\). At \([H_2O] = 0.07\%\), measured \([NO_2]\) ranged from 0 to 291 ppb, whereas at \([H_2O] = 1\%\), measured \([NO_2]\) ranged from 0 to 59 ppb. \([NO_2]\) was lower in the latter case because additional \(OH\) was formed from \(O(1D) + H_2O\) reactions (Section 2.1), which increased the rate of the \(OH + NO_2\) reaction. The mean ratio of modeled-measured \([NO_2]\) was 0.72 ± 0.39 at \([H_2O] = 0.07\%\) and 1.05 ± 0.50 at \([H_2O] = 1\%\). These results, combined with results shown in Figure 1, suggest that an uncharacterized \(H_2O\)- or \(HNO_3\)-related artifact negatively biased the measured \([NO]\) values at \([H_2O] = 1\%\), and that the photochemical model described in Section 2.3 may be used to evaluate a wider range of reactor operating conditions.

### 3.2 Optimal reactor operating conditions for \(O(1D) + N_2O +\) reactions

To investigate optimal operating conditions for \(NO_x\) generation, we implemented the model described in Sect. 2.3 over operating conditions \(I_{254}\), and values ranging from \(3.2 \times 10^{13}\) to \(6.4 \times 10^{15}\) ph cm\(^{-2}\) sec\(^{-1}\), \([O_3]\) = 0.5 to 50 ppm, and \([H_2O]\) = 0.07 to 2.3% at 22°C, respectively, as a function of \([N_2O]\) = 0 to 5%. These values span the nominal range of operating conditions that can be achieved with the PAM reactor. To facilitate independent evaluation of the effects of \([O_3]\) and \(I_{254}\) on \([NO]\), we restricted our analysis to conditions that use only 254 nm photolysis. Using both 185 and 254 nm photolysis provides additional sources of \(O(1D)\) and \(OH\) from \(N_2O\) and \(H_2O\) photolysis at 185 nm, respectively, at the expense of independent control of \([O_3]\) and \(I_{254}\).

Figure 3 shows the modeled steady-state \([NO]\) in the reactor as a function of \([N_2O]\) = 0 to 5%, assuming a mean residence time of 80 sec, \([H_2O]\) = 1%, and \([O_3]\) = 5 ppm. In addition, Figs. S1 - S3 in the Supplement show modeled \(NO:HO_2\) and \(OH:NO_3\) ratios as a function of input \([N_2O]\), with \(I_{254}\), \([O_3]\), and \([H_2O]\) each varied individually while other input conditions are fixed. The following observations that are evident obtained from Figs. 3 and S1 - S3 were used to constrain the optimal oxidant conditions. First, at identify the optimal operating conditions:

1. At fixed \([O_3]\), \([H_2O]\), and \([N_2O]\), increasing \(I_{254}\) increases \(O(1D)\) and consequently \([NO]\). Second, at increase with increasing \(I_{254}\) (Figs. 3 and S1).

2. At fixed \(I_{254}\), \([H_2O]\), and \([N_2O]\), decreasing increasing \(O_3\) increases \(OH\) by decreasing formation from increases the production and loss rates of \(NO\) from \(N_2O + O(1D)\) and \(NO + O_3\) reactions, and consequently formation from respectively. The relative importance of \(NO + OH\), \(NO + O_3\) reactions. At lower, and \(NO + NO_3\) reactions, which depend on \([N_2O]\) and \([O_3]\), further influence \([NO]\):

   - At \([N_2O] \sim 1\%\), increasing \([O_3]\) from 0.5 to 5 ppm increases \([NO]\) because greater \(NO\) production from higher the reaction rate of \(NO + OH\) decreases relative to \(NO + O_3\) (Fig. S2a).

   - At \([N_2O]\) offsets greater \(NO\) loss from reaction with > 1%, increasing \([O_3]\). On the other hand, at higher \([N_2O]\) from 5 to 50 ppm decreases \([NO]\) because the reaction rate of \(NO + NO_3\) increases relative to \(NO + O_3\) (Fig. S2a).
3. At fixed \( I_{254} \), \([H_2O] \), and \([N_2O] \), greater increasing \([O_3] \) losses from reaction with offsets greater NO production from higher.

The relative importance of these operating conditions is situationally dependent on the relative OH, \( O_3 \), and NO rate constants of the target species and photochemical age. To demonstrate proof of principle, we present \( NO_3^- \)-CIMS spectra of isoprene and \( \alpha \)-pinene oxidation products in the following sections.

3.3 \( NO_3^- \)-CIMS spectra of isoprene oxidation products

Figure 4 shows \( NO_3^- \)-CIMS mass spectra of products generated from the oxidation of isoprene \((C_5H_8)\) that cluster with \( NO_3^- \) ions to form \( NO_3^- \)-species adducts. Ion signals are plotted as a function of mass-to-charge ratio \((m/Q)\). \( NO_3^- \) adduct formation is a relatively low-energy process that does not result in fragmentation of the analyte \((\text{Eisele and Tanner, 1993; Kurtén et al., 2011})\). Thus, the measured ion signals are directly related to the chemical formulas of individual species that are generated in the reactor. Ion signals corresponding to isoprene oxidation products shown in Fig. 4 were colored based on classification in ion groups containing \( 4-5 \) carbon atoms with zero \((C_4H_{4-6},O_{4-7} \text{ and } C_5H_{6-8})\), one \((C_2-3H_{3,5}NO_5 \text{ and } C_5H_{7,9,11}NO_{6-11})\), and two \((C_5H_{10}N_2O_{9-10})\) nitrogen atoms, where we assumed that nitrogen atoms were associated with nitrate functional groups and not heterocyclic compounds. We also assume that nitrate functional groups are formed from \( RO_2 + NO \) or \( RO_2 + NO_2 \) reactions \((\text{Sect. 2.1})\). To examine changes in relative contributions of \((C_4H_{4-6},O_{4-7} \text{ and } C_5H_{6-8})\), \( C_5H_{7,9,11}NO_{6-11} \), and \( C_5H_{10}N_2O_{9-10} \) ions as a function of added \( NO_x \), we made two simplifying assumptions: (1) the \( NO_3^- \)-CIMS had the same sensitivity to all species that were detected, and (2) \( HNO_3 \) generated in the reactor did not alter the relative selectivity of the CIMS to different classes of oxidation products, as has been observed in some cases \((\text{Hyttinen et al., 2015})\).

To generate spectra shown in Fig. 4, the reactor was operated at \( I_{254} = 6.4 \times 10^{13} \) and \( 3.2 \times 10^{15} \) ph cm\(^{-2}\) sec\(^{-1}\), \([H_2O] = 1\%\), and \([N_2O] = 0 \text{ and } 3\%\). As shown in Figs. S4 and S5, corresponding OH exposures ranged from \((1.7 - 2.0) \times 10^{10} \) (Fig. 4a and b4c1 calculated \( > 82\% \) of isoprene reacted) and \((0.52 - 2.1) \times 10^{12} \) molec cm\(^{-3}\) sec \((\text{Fig. } 4e \text{ and } \text{d} \text{b and } d4d; \text{calculated } \sim 100\% \text{ of isoprene reacted})\), respectively. At low OH exposure, the OH suppression at “high \( NO_x \)” relative to “low \( NO_x \)” was comparatively minor (15%), whereas at high OH exposure, the OH suppression at “high \( NO_x \)” relative to “low \( NO_x \)” was larger (75%). At the “high-\( NO_x \)” OH exposure of \( 5.2 \times 10^{11} \) molec cm\(^{-3}\) sec, isoprene can react with OH up to 52 times in the reactor. This presumably exceeds the number of OH reactions (followed by \( RO_2 + NO \) reactions) that are necessary to fragment or condense oxidation products to the point where they are no longer detected with \( NO_3^- \)-CIMS. Thus, it is unlikely that OH suppression at “high OH” and “high \( NO_x \)” significantly affected the \( NO_3^- \)-CIMS spectra shown in Fig. 4. To aid interpretation of results shown in Fig. 4, Fig. 5 summarizes several known isoprene + OH reaction pathways that are
terminated by reactions of \( \text{RO}_2 \) with \( \text{HO}_2, \text{NO}_3 \) or \( \text{NO}_2 \). As will be discussed in the following sections, these pathways yield multigenerational oxidation products with chemical formulas corresponding to the major ions that are plotted in Fig. 4.

### 3.3.1 \( \text{NO}_3^- \) CIMS spectral features observed at “low \( \text{NO}_x \)” conditions

\( C_{4–5}H_{1–12}O_{3–8} \) ions comprised 93% and 97% of the signals at low and high OH exposure, respectively (inset pie charts in Figs. 4a and Fig. 4c, respectively). The \( C_5H_{7–11}NO_{6–11} \) signals that were observed here may be due to background \( \text{NO}_x \) in the reactor (Sect. 2.1). The signal at \( m/Q = 230, C_5H_{12}O_6 \) (\( \text{NO}_3^- \) omitted for brevity here and elsewhere), was the largest signal detected at both low and high OH exposures at “low-\( \text{NO}_x \)” conditions. This species is likely Figure 5 suggests this species is a second-generation oxidation product that contains two hydroxyl (OH) and two peroxide (OOH) functional groups generated from two reactions with \( \text{OH} \) and two \( \text{RO}_2 + \text{HO}_2 \) termination reactions (Krechmer et al., 2015; St. Clair et al., 2016) and is typically associated with isoprene SOA formation and growth under “low-\( \text{NO}_x \)” conditions. (Liu et al., 2016) Signals in Figs. 4e-d-b and 4d are approximately 10 times higher than in Figs. 4a-b-a and 4c because additional OH exposure produces higher yields of multi-generation oxidation products that are detected with \( \text{NO}_3^- \) CIMS.

Previously-identified multi-generation isoprene oxidation products such as \( C_5H_{10}O_5, C_5H_{12}O_5 \), and \( C_5H_{10}O_6 \) (Surratt et al., 2006; Krechmer et al., 2015; St. Clair et al., 2016) were also detected at significant intensity under low-\( \text{NO}_x \) conditions. These species are formed after two reactions with \( \text{OH} \), one \( \text{RO}_2 + \text{HO}_2 \) termination reaction and one \( \text{RO}_2 + \text{RO}_2 \) termination reaction (Fig. 5). When the OH exposure was increased by a factor of 100 from \( 2.0 \times 10^{10} \) to \( 2.1 \times 10^{12} \) molec cm\(^{-3} \) sec, the signal at \( C_5H_{12}O_6 \) increased by a factor of 10 and the signal at \( m/Q = 246, C_5H_{12}O_7 \), increased by a factor of 5. At high OH exposure, \( C_5H_{12}O_7 \) was the second-largest peak in the spectrum. These highly oxygenated isoprene oxidation products are likely also important in SOA formation processes. We note that \( C_5H_{10}O_7 \) is a proposed third-generation, tri-hydroperoxy carbonyl product of isoprene + \( \text{OH} \) (in the absence of (Peeters et al., 2014)-formed after one reaction with \( \text{OH} \), two hydrogen shifts and one \( \text{RO}_2 + \text{HO}_2 \) termination reaction as shown in Fig. 5 (Peeters et al., 2014).

We hypothesize two reasons for the prominence of \( C_5H_{10}O_7, C_5H_{12}O_7 \), and \( C_5H_{10}O_8 \) in our spectra. First, \( \text{NO}_3^- \) is more selective to highly oxidized species than other reagent ions (Surratt et al., 2006; Liu et al., 2016). Second, higher OH exposures were achieved in the reactor than in environmental chambers. For example, the spectra shown in Figs. 4a and 4b were obtained at integrated OH exposures of \( 1.7 \times 10^{10} \) and \( 2.1 \times 10^{12} \) molec cm\(^{-3} \) sec, respectively, compared to an OH exposure of \( 8.6 \times 10^9 \) molec cm\(^{-3} \) sec in the environmental chamber \( \text{NO}_3^- \) CIMS measurements conducted by Krechmer et al. (2015).

### 3.3.2 \( \text{NO}_3^- \) CIMS spectral features observed at “high \( \text{NO}_x \)” conditions

Following addition of \( \text{N}_2\text{O} \) at \( \sim 3\% \) mixing ratio, the \( \text{NO}_3^- \) CIMS spectra changed significantly at low and high OH exposures (Figs. 4b and 4d). The signals of \( C_{4–5}H_{4–12}O_{3–8} \) oxidation products decreased, and the signals of although the

\( C_4H_{4,6,8}O_{4–7}, C_5H_{6,8,10,12}O_{3–8} \) ratio increased, presumably due to decomposition of alkoxy (RO) radicals generated from \( \text{C}_5 \) \( \text{RO}_2 + \text{NO} \) reactions into \( \text{C}_4 \) products. The \( \text{C}_2–\text{C}_3\text{H}_3\text{H}_2\text{NO}_5 \) (peroxy acetyl nitrate and peroxy propionyl nitrate), \( C_5H_{7,9,11}NO_{6–11} \) and oxidation products \( C_5H_{10}N_2O_8–10 \) signals increased. At low OH exposure, and signals constituted 24% and 8\% \( \text{C}_2–\text{C}_3\text{H}_3\text{N}_2\text{O}_5, C_5H_{7,9,11}NO_{6–11} \) and \( C_5H_{10}N_2O_8–10 \) signals constituted 2\%, 38\% and 7\% of the \( \text{NO}_3^- \) CIMS
signals, respectively (Fig. 4). The largest signal in this spectrum was m/Q = 259. This compound is likely \( \text{C}_5\text{H}_{11}\text{NO}_7 \). Fig. 5 suggests this compound is a second-generation oxidation product that contains two hydroxyl functional groups and one nitrate functional group (Xiong et al., 2015). A series of additional ions is also detected, is formed after two reactions with OH, one RO\(_2\) + NO termination reaction and one RO\(_2\) + HO\(_2\) termination reaction (Xiong et al., 2015). The signal observed at m/Q = 288, is likely C\(_5\)H\(_{10}\)N\(_2\)O\(_8\), is a second-generation oxidation product that contains two hydroxyl and two nitrate functional groups is formed after two reactions with OH and two RO\(_2\) + NO termination reactions (Fig. 5) (Xiong et al., 2015). Other ion signals potentially associated with dinitrate species included m/Q = 304, C\(_5\)H\(_{10}\)N\(_2\)O\(_9\), and m/Q = 320, C\(_5\)H\(_{10}\)N\(_2\)O\(_{10}\). Related signals were detected at m/Q = 351 and 367 (not shown), which we assume represent (HNO\(_3\)NO\(_3\))C\(_5\)H\(_{10}\)N\(_2\)O\(_8\) and (HNO\(_3\)NO\(_3\))C\(_5\)H\(_{10}\)N\(_2\)O\(_9\) because we are not aware of other feasible (NO\(_3\))C\(_5\) adducts at these mass-to-charge ratios.

At high OH exposure, the same and C\(_5\)H\(_{7,9,11}\)NO\(_6\)−11 and C\(_5\)H\(_{10}\)N\(_2\)O\(_8\)−10 species observed at low OH exposure were detected, but at higher concentrations and at higher dinitrate:nitrate. This is presumably due to higher NO:HO\(_2\) achieved at higher I\(_{254}\) and fixed [N\(_2\)O] (Figs. 3, S\(_1\), S\(_4\)-S\(_5\), and S\(_2\), S\(_5\)-S\(_6\)). C\(_2\)−3H\(_3,5\)NO\(_5\), C\(_5\)H\(_{7,9,11}\)NO\(_6\)−11, and C\(_5\)H\(_{10}\)N\(_2\)O\(_8\)−10 signals made up 30%, 33%, and 56%, respectively, of the NO\(_3^−\)-CIMS spectrum shown in Fig. 4d, where C\(_5\)H\(_{10}\)N\(_2\)O\(_8\) was the largest signal that is detected.

To demonstrate our ability to mimic atmospheric NO\(_x\)-dependent photochemistry, Figures 4e and 4f show C\(_4\)H\(_{4,6,8}\)O\(_{4−7}\), C\(_5\)H\(_{6,8,10,12}\)O\(_{3−8}\), C\(_2\)−3H\(_3,5\)NO\(_5\), C\(_5\)H\(_{7,9,11}\)NO\(_6\)−11, and C\(_5\)H\(_{10}\)N\(_2\)O\(_8\)−10 ion signals detected in NO\(_3^−\)-CIMS spectra at the SOAS ground site in Centreville, Alabama, USA. The spectra shown were obtained on 25 Jun 2013 (0730–1100) and 4–5 Jul 2013 (1200 – 0000) which represented periods with sustained “high” and “low” NO mixing ratios of 0.53 ± 0.17 ppb and 0.024 ± 0.025 ppb, respectively, measured at the site. Figures 4a, 4c and 4e indicate that adding N\(_2\)O to the reactor increases the similarity between the composition of isoprene oxidation products generated at lower photochemical age in the reactor (Figs. 4a and 4c) and under “low-NO” ambient conditions (Fig. 4e). Likewise, Figures 4b, 4d and 4f indicate that adding N\(_2\)O to the reactor increases the similarity between the composition of isoprene oxidation products generated at higher photochemical age in the reactor (Figs. 4b and 4d) and at “high-NO” ambient conditions (Fig. 4f). (HNO\(_3\)NO\(_3^−\))C\(_5\)H\(_{10}\)N\(_2\)O\(_8\)−9 adducts were also observed in Fig. 4f (not shown).

### 3.3.3 Influence of acylyperoxy nitrates from RO\(_2\) + NO\(_2\) reactions

Acylperoxy nitrates (APNs) may be generated from reactions of aldehydic, biogenic VOC oxidation products with OH followed by RO\(_2\) + NO\(_2\) termination reactions, e.g. LaFranchi et al. (2009). Peroxy acetyl nitrate (PAN, C\(_2\)H\(_3\)NO\(_5\)) and propionyl peroxy nitrate (PPN, C\(_3\)H\(_5\)NO\(_5\)), are minor components (<2%) of the spectra shown in Figs. 4e - 4f. A comparison of Figs. 4e and 4f suggests that yields of PAN and PPN are not enhanced in the reactor compared to atmospheric conditions.

Additional APNs may be generated following the OH oxidation of methacrolein, a first-generation isoprene oxidation product. Methacryloyl peroxy nitrate (MPAN, C\(_4\)H\(_5\)NO\(_5\)) is a second-generation oxidation product formed after one methacrolein + OH reaction and one RO\(_2\) + NO\(_2\) termination reaction (Orlando et al., 1999). C\(_4\)-hydroxynitrate-PAN (C\(_4\)H\(_6\)N\(_2\)O\(_9\)) is a third-generation oxidation product formed through the methacrolein channel after three reactions with OH, two RO\(_2\) + NO termination reactions and one RO\(_2\) + NO\(_2\) termination reaction (Surratt et al., 2010). Neither C\(_4\)H\(_5\)NO\(_5\) nor C\(_4\)H\(_6\)N\(_2\)O\(_9\) were
detected in the laboratory and ambient NO$_3^-$-CIMS spectra shown in Figs. 4c - 4f. Either these compounds were oxidized or thermally decomposed prior to detection, or their signals were below detection limit. C$_4$H$_7$NO$_5$, which is formed after one methacrolein + OH reaction and one RO$_2$ + NO termination reaction (Surratt et al., 2010), was detected (Fig. 5). Taken together, these observations suggest that yields of APNs were not significantly enhanced in the reactor compared to atmospheric conditions.

3.3.4 Influence of isoprene + NO$_3^-$ reactions

Based on the calculated isoprene + OH and isoprene + NO$_3^-$ reaction rates (Figs. S5-S6) we assume that isoprene + NO$_3^-$ reactions were a minor influence on the NO$_3^-$-CIMS spectra shown in Figs. 4c and 4d. This assumption is further supported by the similarity between laboratory and ambient NO$_3^-$-CIMS spectra, the latter of which was obtained during the daytime and thus with minimal NO$_3^-$ exposure (0730 - 1100 for “high-NO” spectra shown in Fig. 4f). Specific operating conditions different than those used in this study could increase the relative influence of isoprene + NO$_3^-$ reactions. In this hypothetical situation, enhanced yields of C$_5$H$_7$NO$_5$, C$_5$H$_8$N$_2$O$_8$ and C$_5$H$_{10}$N$_2$O$_8$ might occur following two reactions with NO$_3^-$ (Rollins et al., 2009). In addition, C$_5$H$_{10}$N$_2$O$_9$ may be generated from one isoprene + NO$_3^-$ reaction followed by one RO$_2$ + HO$_2$ termination reaction (Schwantes et al., 2015). All four of these ions are detected in the spectra shown in Fig. 4, although C$_5$H$_8$N$_2$O$_8$ (not shown in Fig. 4) is present at 0.5% of the intensity of C$_5$H$_{10}$N$_2$O$_8$. If C$_5$H$_8$N$_2$O$_8$ : C$_5$H$_{10}$N$_2$O$_8$ is significantly different under NO$_3^-$-dominated conditions, this ratio could distinguish the relative rates of isoprene + OH and isoprene + NO$_3^-$ reactions. Otherwise, it is not clear that the expected product distributions are significantly different whether isoprene is oxidized by OH or NO$_3^-$ in the presence of NO$_x$.

3.4 NO$_3^-$-CIMS spectra of α-pinene oxidation products

Figure 6 shows NO$_3^-$-CIMS mass spectra of products generated from the oxidation of α-pinene (C$_{10}$H$_{16}$). Ion signals corresponding to α-pinene oxidation products were colored based on classification in C$_{5}$H$_{5}$O$_{5}$-7, C$_{6}$-9H$_{8}$,10,12,14O$_{6}$-12, C$_{10}$H$_{14}$,16,18O$_{5}$-14, and C$_{19}$-20H$_{28}$,30,32O$_{9}$-18 ion groups containing zero nitrogen atoms; and C$_{2}$-3H$_{3}$,5NO$_{5}$, C$_{5}$H$_{7}$NO$_{6}$-11, C$_{6}$-9H$_{9}$,11,13,15NO$_{5}$-10, and C$_{10}$H$_{15}$,17NO$_{4}$-14 ion groups containing one nitrogen atom; and a C$_{10}$H$_{16}$,18N$_{2}$O$_{6}$-13 ion group containing two nitrogen atoms. As was the case with isoprene oxidation products, we assumed nitrogen atoms present in α-pinene oxidation products were associated with nitrate functional groups formed from RO$_2$ + NO reactions or RO$_2$ + NO$_2$ reactions. Additionally, we again assumed the NO$_3^-$-CIMS had the same sensitivity to all species that were detected, and that HNO$_3$ generated in the reactor did not alter the relative selectivity of the CIMS to different classes of oxidation products. Because the oxidation pathways leading to α-pinene-derived HOM are significantly more complex than those leading to isoprene-derived HOM, the analogous figure to Fig. 5 for α-pinene-derived HOM is beyond the scope of this paper.

To generate spectra shown in Fig. 6, the reactor was operated at I$_{254} = 2.8 \times 10^{15}$ ph cm$^{-2}$sec$^{-1}$, [H$_2$O] = 0.07%, and [N$_2$O] = 0 and 3.2%. In this experiment, lower [H$_2$O] was used to minimize [OH] and facilitate closer comparison with spectra from previous NO$_3^-$-CIMS studies of α-pinene + O$_3$ oxidation products generated at “low-NO$_x$” conditions (Ehn et al., 2012,
comprised, and ion signal in Fig. 6b was observed at \( m/Q = 240 \), signals that were observed correspond to \( \text{C} \) and ion, carbon group(s).

\[ \text{C}6\% \text{C} \]

As was the case with \( \text{NO}_3^- \)-CIMS were minimized relative to \( \alpha \)-pinene + \( \text{O}_3 \) first-generation oxidation products, as desired (Jokinen et al., 2015). However, a potential consequence of using \( \text{O}^{(1D)} \) + \( \text{N}_2\text{O} \) reactions to study the \( \text{NO}_x \)-dependence of chemical systems similar to those examined by Ehn et al. (2012, 2014) is that \( \text{RO}_2 \) may be produced from \( \alpha \)-pinene + \( \text{NO}_3 \) reactions in addition to \( \alpha \)-pinene + \( \text{O}_3 \) or \( \alpha \)-pinene + \( \text{OH} \) reactions (Sect. 2.1 and Fig. S6–S7).

3.4.1 \( \text{NO}_3^- \)-CIMS mass spectral features observed at “low \( \text{NO}_x \)” conditions

Of \( \text{C}_5\text{H}_6\text{O}_5\text{O}_7\text{H}_8\text{O}_9\text{O}_{10-14}\text{O}_{15-14} \) and \( \text{C}_{19-20}\text{H}_{28,30,32}\text{O}_{9-18} \) ion groups comprised 5%, 36%, 46%, and 4% of the signal detected at “low-\( \text{NO}_x \)” conditions (Fig. 6a), and ion groups comprised 6%, 23%, 54%, and 5%, respectively assuming equal CIMS sensitivity and transmission to all detected species. The \( \text{C}_{10} \) monomers and \( \text{C}_{19-20} \) dimers compounds that were observed are often associated with atmospheric new particle formation events (Ehn et al., 2014).

The prominent \( \text{C}_{10}\text{H}_{14,16}\text{O}_{7-9} \) ion signals detected at \( m/Q = 308, 310, 324, 326, 340 \) and 342 in our measurements were dominant signals in previous laboratory and field experiments influenced by the ozonolysis of \( \alpha \)-pinene emissions (Ehn et al., 2010, 2012, 2014; Jokinen et al., 2015). Other ion signals that were observed correspond to \( \text{C}_{5-9} \) species that were generated following carbon-carbon bond cleavage of the \( \text{C}_{10} \) carbon-backbone (Ehn et al., 2012). The remaining \( \sim 13 \% \) of the signal was classified into and \( \text{C}_{2-3}\text{H}_{3,5}\text{NO}_{5-10} \), \( \text{C}_{5}\text{H}_{7}\text{NO}_{6-11} \), \( \text{C}_{6-9}\text{H}_{9,11,13,15}\text{NO}_{5-10} \), and \( \text{C}_{10}\text{H}_{15,17}\text{NO}_{1-14} \) ion groups and may be due to background \( \text{NO}_x \) in the reactor (Sect. 2.1).

3.4.2 \( \text{NO}_3^- \)-CIMS mass spectral features observed at “high \( \text{NO}_x \)” conditions

As was the case with \( \text{NO}_3^- \)-CIMS spectra of isoprene oxidation products, the addition of \( \text{N}_2\text{O} \) to the reactor significantly changed the mass spectrum of \( \alpha \)-pinene oxidation products (Fig. 6b). At \([\text{N}_2\text{O}] = 3.2\%\), organic nitrates and dinitrates comprised 65% of the total ion signal (Fig. 6b inset). We observed reduction in and ion \( \text{C}_{6-9}\text{H}_{8,10,12,14}\text{O}_{6-12} \), \( \text{C}_{10}\text{H}_{14,16,18}\text{O}_{5-14} \), and \( \text{C}_{19-20}\text{H}_{28,30,32}\text{O}_{9-18} \) signals, along with increases in and \( \text{C}_{5}\text{H}_{6,8}\text{O}_{5-7} \), \( \text{C}_{5}\text{H}_{7}\text{O}_{6-11} \), \( \text{C}_{6-9}\text{H}_{9,11,13,15}\text{NO}_{5-10} \), \( \text{C}_{10}\text{H}_{15,17}\text{NO}_{4-14} \), and \( \text{C}_{10}\text{H}_{16,18}\text{N}_{2}\text{O}_{6-13} \) signals. The \( \text{C}_{10} \) dinitrates may originate from two \( \alpha \)-pinene + \( \text{OH} \) reactions followed by two \( \text{RO}_2 + \text{NO} \) reactions, but may also include contributions from one \( \alpha \)-pinene + \( \text{NO}_3 \) reaction followed by one \( \text{RO}_2 + \text{NO} \) reaction. The largest ion signal in Fig. 6b was observed at \( m/Q = 240 \), \( \text{C}_{5}\text{H}_{6}\text{O}_7 \). The largest organic nitrate signals in this spectrum were at \( m/Q = 329 \), \( \text{C}_{8}\text{H}_{13}\text{NO}_9 \), followed by \( \text{C}_{10}\text{H}_{15}\text{NO}_9 \) (\( m/Q = 355 \)), \( \text{C}_{10}\text{H}_{16}\text{N}_2\text{O}_9 \) (\( m/Q = 354 \)), and \( \text{C}_{10}\text{H}_{15}\text{NO}_8 \) (\( m/Q = 339 \)).

Figure 6c shows \( \text{C}_{5}\text{H}_{6}\text{O}_{5-7} \), \( \text{C}_{6-9}\text{H}_{8,10,12,14}\text{O}_{6-12} \), \( \text{C}_{10}\text{H}_{14,16,18}\text{O}_{5-14} \), \( \text{C}_{19-20}\text{H}_{28,30,32}\text{O}_{9-18} \), \( \text{C}_{2-3}\text{H}_{3,5}\text{NO}_5 \), \( \text{C}_{5}\text{H}_{7}\text{NO}_6-11 \), \( \text{C}_{6-9}\text{H}_{9,11,13,15}\text{NO}_5-10 \), \( \text{C}_{10}\text{H}_{15,17}\text{NO}_4-14 \), and \( \text{C}_{10}\text{H}_{16,18}\text{N}_{2}\text{O}_6-13 \) signals detected with \( \text{NO}_3^- \)-CIMS at the Centreville site during the SOAS campaign. The spectra shown here were obtained during the sampling period shown in Fig. 4f and, given
the large number of compounds, may include contributions from HOM precursors other than \( \alpha \)-pinene. A comparison of Figs. 6a-6c indicates that adding \( N_2O \) to the reactor increases the similarity between the composition of \( \alpha \)-pinene oxidation products generated in the reactor and under “high-NO” ambient conditions, especially in regards to the enhanced \( C_5H_6O_5-7 \), \( C_6-9H_{9,11,13,15}NO_5-10 \), \( C_{10}H_{15,17}NO_4-14 \), and \( C_{10}H_{16,18}N_2O_6-13 \) signals.

3.4.3 Detection of acyloperoxy nitrates from \( RO_2 + NO_2 \) reactions

Figs. 6b and 6c indicate that PAN (m/Q = 183, \( C_2H_3NO_5 \)) and PPN (m/Q = 197, \( C_3H_5NO_5 \)) are formed at lower yields (<0.4%) than were observed with isoprene (Fig. 4c and 4d), suggesting that PAN and PPN formation from reaction of \( \alpha \)-pinene-derived–RO\(_2\) with \( NO_2 \) are not enhanced in the reactor compared to atmospheric conditions. \( C_9H_{13}NO_6 \) and \( C_{10}H_{15}NO_6-8 \) are APNs generated following OH oxidation of pinonaldehyde, a major first-generation oxidation product of \( \alpha \)-pinene, with termination by \( RO_2 + NO_2 \) reaction (Eddingsaas et al., 2012). All four compounds are detected in the reactor and ambient \( NO_3^- \)-CIMS spectra shown in Figs. 6b and 6c, with \( C_{10}H_{15}NO_6-8 \) signals among the largest in the spectra. If these signals represent APNs, they appear to be important in both laboratory and atmospheric conditions.

3.4.4 Influence of \( \alpha \)-pinene + \( NO_3^- \) reactions

Our calculations suggest that \( \alpha \)-pinene + \( NO_3^- \) reactions compete with \( \alpha \)-pinene + OH reactions at the experimental conditions used to generate the \( NO_3^- \)-CIMS spectrum shown in Fig. 6b (Fig. S7). If this were the case, enhanced yields of \( C_{10}H_{15}NO_6 \) are anticipated from \( \alpha \)-pinene + \( NO_3^- \) reaction to generate pinonaldehyde, followed by pinonaldehyde + \( NO_3^- \) reaction and \( RO_2 + NO_2 \) termination (Perraud et al., 2010; Nah et al., 2016). Other minor \( \alpha \)-pinene + \( NO_3^- \) products detected with CIMS include \( C_{10}H_{15}NO_5 \), \( C_9H_{13}NO_6 \), \( C_{10}H_{16}N_2O_7 \), and \( C_{10}H_{15}NO_9 \) (Nah et al., 2016). We hypothesize that if \( \alpha \)-pinene + \( NO_3^- \) reactions influence the spectrum shown in Fig. 6b, \( C_{10}H_{15}NO_6 : C_{10}H_{15}NO_8 \) should be higher in Fig. 6b than in Fig. 6c.

Instead, the \( C_{10}H_{15}NO_6 : C_{10}H_{15}NO_8 \) ratio was 0.12 in the reactor and 0.28 at the Centreville site during a daytime period (0730 - 1100) with presumably negligible \( NO_3^- \) influence.

Dinitrates (\( C_{10}H_{16,18}N_2O_6-13 \)) shown in Fig. 6b may originate from two \( \alpha \)-pinene + OH reactions followed by two \( RO_2 + NO \) terminations, or one \( \alpha \)-pinene + \( NO_3^- \) reaction followed by one \( RO_2 + NO \) termination. Given comparable calculated OH and \( NO_3^- \) reaction rates under these conditions (Fig. S7c), we hypothesize that the majority of dinitrate signals should originate from \( \alpha \)-pinene + \( NO_3^- \) reactions if their yields are not oxidant-dependent. If this were the case, \( C_{10}H_{16,18}N_2O_6-13 \), \( C_{10}H_{15,17}NO_4-14 \) should be larger in Fig. 6b than in Fig. 6c. However, \( C_{10}H_{16,18}N_2O_6-13 \), \( C_{10}H_{16,18}N_2O_6-13 \), and \( C_{10}H_{16,18}N_2O_6-13 \) were 0.23 in the reactor and 0.61 at the Centreville site. Thus, while the calculated \( \alpha \)-pinene + \( NO_3^- \) oxidation rate is significant (Fig. S7e), it is not clear that \( \alpha \)-pinene + \( NO_3^- \) oxidation products significantly affect the spectrum shown in Fig. 6b. This may be due to significantly lower organic nitrate yields from \( \alpha \)-pinene + \( NO_3^- \) than from \( \alpha \)-pinene + OH reactions in the presence of NO (Fry et al., 2014; Rindelaub et al., 2015).
3.5 Transition from $\text{RO}_2+\text{HO}_2$ to $\text{RO}_2+\text{NO}$-dominant regimes observed in isoprene and $\alpha$-pinene oxidation products

Figures 7 and 8 shows normalized signals of the representative groups of isoprene and $\alpha$-pinene oxidation products as a function of increasing $\text{NO}:\text{HO}_2$, which may be influenced by $\text{NO}+\text{HO}_2$, $\text{NO}+\text{RO}_2$ and $\text{HO}_2+\text{RO}_2$ reactions in the reactor. For each group of compounds, signals obtained at a specific $\text{NO}:\text{HO}_2$ were normalized to the maximum observed signal. $\text{NO}:\text{HO}_2$ is correlated with the relative branching ratios of $\text{RO}_2+\text{HO}_2$ and $\text{RO}_2+\text{NO}$ reactions that govern the distribution of oxidation products observed in Figs. 4 and 6. As is evident from Figs. 7 and 8, different ion families were characterized by different trends as a function of $\text{NO}:\text{HO}_2$. The normalized signals of $\text{C}_{4-5}$ (isoprene), $\text{C}_{6-10}$ ($\alpha$-pinene) and $\text{C}_{19-20}$ ($\alpha$-pinene) species decreased monotonically with increasing $\text{NO}:\text{HO}_2$. In Fig. 8, the abundance of $\text{C}_{19-20}$ dimers decreased significantly faster than the $\text{C}_{6-10}$ species. Because dimers are products of $\text{RO}_2+\text{RO}_2$ self-reactions, their yield is quadratic with respect to [RO$_2$] and therefore was more affected by competing RO$_2$ + NO reactions than species formed from RO$_2$ + HO$_2$ reactions.

The normalized signals of $\text{C}_5$ (isoprene) and $\text{C}_{10}$ ($\alpha$-pinene) organic nitrates reached their maximum values at $\text{NO}:\text{HO}_2 \approx 1$ prior to decreasing. Maximum signals of $\text{C}_{6-9}$ organic nitrates ($\alpha$-pinene) were obtained at $\text{NO}:\text{HO}_2 = 2.4$, and maximum signals of $\text{C}_5$ (isoprene) and $\text{C}_{10}$ ($\alpha$-pinene) dinitrates were obtained at $\text{NO}:\text{HO}_2 = 5.2$ and 6.4. The formation of dinitrates was favored when $\text{RO}_2 + \text{NO} >> \text{RO}_2 + \text{HO}_2$, as expected, and regardless of whether $\text{RO}_2$ was formed from oxidation of $\alpha$-pinene by OH, O$_3$ or NO$_3$. We hypothesize that $\text{NO}:\text{HO}_2 \approx 1$ favored $\text{RO}_2 + \text{NO} \rightarrow \text{RO} + \text{NO}_2$ fragmentation reactions that led to formation of smaller, more volatile $\text{C}_5\text{H}_6\text{O}_5\text{O}_7$ and $\text{C}_5\text{H}_7\text{NO}_6\text{O}_6\text{O}_7$ $\alpha$-pinene oxidation products (Atkinson, 2007; Chacon-Madrid and Donahue, 2011), whose signals continuously increased with increasing $\text{NO}:\text{HO}_2$, along with other products not detected with NO$_3$-CIMS. This pathway apparently competed with influenced auto-oxidation processes $\text{RO}_2 + \text{NO} \rightarrow \text{RO}_2\text{NO}$ reactions that led to formation of $\text{C}_5$ isoprene dinitrates, $\text{C}_6$-$\text{C}_{10}$ $\alpha$-pinene nitrates and $\text{C}_{10}$ $\alpha$-pinene dinitrates.

Isoprene oxidation products such as $\text{C}_5\text{H}_9\text{NO}_7$ and $\text{C}_5\text{H}_{11}\text{NO}_7$ contain one peroxide and one nitrate functional group, and contains two peroxide $\text{C}_5\text{H}_9\text{NO}_8$ contains two peroxides and one nitrate functional group. The formation of these species, as well as $\text{C}_{6-10}$ $\alpha$-pinene-derived organic nitrates, was favored at $\text{NO}:\text{HO}_2 \approx 1-2$ where the relative rates of $\text{RO}_2 + \text{NO}$ and $\text{RO}_2 + \text{HO}_2$ reactions were similar. This correlation suggests that the $\text{C}_{6-10}$ $\alpha$-pinene organic nitrates detected with NO$_3$-CIMS contained a combination of peroxide and nitrate functional groups, whereas $\text{C}_5$ (isoprene) and $\text{C}_{10}$ ($\alpha$-pinene) dinitrates contained fewer functional groups that were specifically formed from $\text{RO}_2 + \text{HO}_2$ reactions.

4 Atmospheric Implications

The use of $\text{O}^\text{(1)}\text{D} + \text{N}_2\text{O}$ reactions in oxidation flow reactors facilitates systematic control of $\text{NO}:\text{HO}_2$ over the range of “$\text{RO}_2 + \text{HO}_2$ dominant” to “$\text{RO}_2 + \text{NO}$ dominant” conditions. Further, this is accomplished with the use of a single OH radical precursor (O$_3$) that has previously hindered characterization of NO$_x$-dependent chemistry in oxidation flow reactors. Our results suggest that this method can be used to identify molecular tracers for processes influenced by $\text{RO}_2 + \text{NO}$ and/or $\text{RO}_2 + \text{NO}_2$ reactions. For example, compounds formed from the oxidation of isoprene were detected in air masses influenced by mixed isoprene and anthropogenic emissions (Lee et al., 2016). Similarly, compounds formed from the oxidation of $\alpha$-pinene
were detected in air masses influenced by α-pinene emissions that were subsequently oxidized by in the presence of NO (Yan et al., 2016).

(Figs. 4 and 6). This method will be used in future work to investigate the influence of NOx on physicochemical properties of secondary organic aerosols such as hygroscopicity and refractive indices over an atmospherically relevant range of NO:HO2.

Care should be taken to use experimental conditions that minimize the relative contributions of unwanted NO3-initiated oxidation chemistry, particularly when using species such as α-pinene that are highly reactive to NO3. While potential formation of dinitrates from α-pinene + NO3 reactions at high-NO conditions was not the primary goal of this experiment, we note that this chemical fingerprint has been observed in ambient measurements (Yan et al., 2016) and thus represents an additional application of O(1D) + N2O reactions in future work. Additionally, studies that require multiple days of equivalent atmospheric OH oxidation at NO:HO2 >> 1 should consider implementing 185 nm photolysis of H2O and N2O to provide additional sources of O(1D) and OH that may decrease OH suppression due to competing O(1D) + H2O and O(1D) + N2O reactions.

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References


Figure 1. Scatter plot comparing measured and modeled [NO] at 80 sec residence time in the PAM oxidation flow reactor, $I_{254} = 4 \times 10^{15}$ ph cm$^{-2}$ sec$^{-1}$, $[O_3] = 1$ ppm, $[H_2O] = 0.07$% and 1%, $[N_2O] = 0$ to 3%. Symbols are colored by $[N_2O]$, with 1:2, 1:1 and 2:1 lines shown for reference. Error bars represent ±60% uncertainty in model outputs (Peng et al., 2015) and ±40% precision in replicate [NO] measurements at fixed $[N_2O]$. 
Figure 2. Scatter plot comparing measured and modeled [NO$_2$] at 80 sec residence time in the PAM reactor, $I_{254} = 4 \times 10^{15}$ ph cm$^{-2}$ sec$^{-1}$, [O$_3$] = 1 ppm, [H$_2$O] = 0.07% and 1%, [N$_2$O] = 0 to 3%. Symbols are colored by [N$_2$O], with 1:2, 1:1 and 2:1 lines shown for reference. Error bars represent ±60% uncertainty in model outputs (Peng et al., 2015) and ±20% precision in replicate [NO] measurements at fixed [N$_2$O].
**Figure 3.** Modeled steady-state [NO] as a function of [N$_2$O] input to the PAM oxidation flow reactor at $I_{254} = 0.032 \times 10^{15}$, $0.64 \times 10^{15}$ and $6.4 \times 10^{15}$ ph cm$^{-2}$ sec$^{-1}$, [H$_2$O] = 1%, [O$_3$] = 5 ppm, mean residence time = 80 sec. Error bars represent ± 60% uncertainty in modeled [NO] (Peng et al., 2015).
**Figure 4.** NO$_3^-$-CIMS mass spectra of isoprene oxidation products generated in the PAM reactor at [H$_2$O] = 1%, [O$_3$] = 5 ppm, mean residence time = 80 sec: (a) I$_{254}$ = 6.4×10$^{13}$ ph cm$^{-2}$ sec$^{-1}$, [N$_2$O] = 0%; (b) I$_{254}$ = 6.43×10$^{13}$ ph cm$^{-2}$ sec$^{-1}$, [N$_2$O] = 0.2%; (c) I$_{254}$ = 3.26×10$^{15}$ ph cm$^{-2}$ sec$^{-1}$, [N$_2$O] = 0.32%; (d) I$_{254}$ = 3.2×10$^{15}$ ph cm$^{-2}$ sec$^{-1}$, [N$_2$O] = 2.9%. Colors are based on classification NO$_3^-$-CIMS mass spectra of the same compounds detected at the SOAS ground site in Centreville, Alabama, USA during (e) “low-NO” and (f) “high-NO” conditions (see text for additional details; C$_5$H$_6$O$_{5-7}$ ions removed from SOAS spectra due to larger contributions indicated in inset pie charts from α-pinene + OH oxidation products (brown outline = organonitrate Fig. 6). “C$_{x}$” or “O$_{x}$” indicates number of oxygen or carbon atoms in labeled ions (not including oxygen atoms in nitrate functional groups).
Figure 5. Simplified reaction scheme summarizing known isoprene + OH reaction pathways yielding multigeneration oxidation products. Four peroxo radical (RO₂) isomers are generated following initial OH addition to isoprene: 1,2-RO₂, 4,3-RO₂, 1,4-RO₂, and 4,1-RO₂. The 1,2-RO₂ and 4,3-RO₂ isomers follow the same reaction pathways, yielding chemical formulas with green text that were detected with NO₃⁻-CIMS. The 4,1-RO₂ isomer yields C₅H₁₀O₇, also detected with NO₃⁻-CIMS. Chemical formulas with red text may be generated through the methacrolein (MACR) channel but were not detected with NO₃⁻-CIMS.
Figure 6. $\text{NO}_3^-$-CIMS mass spectra of $\alpha$-pinene oxidation products generated in the PAM reactor at $[\text{H}_2\text{O}] = 0.07\%$, $[\text{O}_3] = 5$ ppm, mean residence time = 80 sec; (a) $I_{254} = 2.8 \times 10^{15}$ ph cm$^{-2}$sec$^{-1}$, $[\text{N}_2\text{O}] = 0$%; (b) $I_{254} = 2.8 \times 10^{15}$ ph cm$^{-2}$sec$^{-1}$, $[\text{N}_2\text{O}] = 3.2$%. (c) $\text{NO}_3^-$-CIMS mass spectra of the same compounds detected at the SOAS ground site in Centreville, Alabama, USA during “high-NO” conditions shown in Fig. 4f (note: $C_5H_7NO_{6-11}$ signals in SOAS spectra also contributed from isoprene + OH oxidation products). “$C_x$” or “$O_x$” labels indicate number of oxygen atoms in corresponding signals (not including oxygen atoms in nitrate functional groups).
Figure 7. Normalized NO$_3^-$-CIMS signals of C$_4$H$_{4,6,8}$O$_{4-7}$, C$_5$H$_{6,8,10,12}$O$_{3-8}$, C$_5$H$_{7,9,11}$NO$_{6-11}$, and C$_5$H$_{10}$N$_2$O$_{8-10}$ isoprene oxidation products generated in the PAM reactor at I$_{254} = 3.2 \times 10^{15}$ ph cm$^{-2}$ sec$^{-1}$, [H$_2$O] $\approx$ 1%, [O$_3$] $\approx$ 5 ppm, mean residence time $= 80$ sec as a function of modeled NO:HO$_2$. For each of the species classes, signals were normalized to the maximum signal. Proposed structures for C$_5$H$_{12}$O$_6$, C$_5$H$_{11}$NO$_7$, and C$_5$H$_{10}$N$_2$O$_8$ signals are shown as representative compounds for each species class (Fig. 5). Representative error bars indicate ± 1σ uncertainty in NO$_3^-$-CIMS signals and ± 85% uncertainty in NO:HO$_2$. 

29
Figure 8. Normalized NO₃⁻-CIMS signals of (a) C₅H₆,O₅−₇, C₆−9H₈,10,12,14O₆−₁₂, C₁₀H₁₄,16,18O₅−₁₄, C₁₉−₂₀H₂₈,3₀,3₂O₉−₁₄ and (b) C₅H₇NO₆−₁₁, C₆−9H₉,₁₁,₁₃,₁₅NO₅−₁₀, C₁₀H₁₅,₁₇NO₄−₁₄, and C₁₉H₁₆,₁₈N₂O₆−₁₃ α-pinene oxidation products generated in the PAM reactor at I₂₅₄ = 2.8 × 10¹⁵ ph cm⁻² sec⁻¹, [H₂O] = 0.07%, [O₃] = 5 ppm, mean residence time = 80 sec as a function of modeled NO:HO₂. For each of the species classes, signals were normalized to the maximum signal. Representative error bars indicate ± 1σ uncertainty in NO₃⁻-CIMS signals and ± 85% uncertainty in modeled NO:HO₂.
Figure S1. Nitric oxide (NO) depletion inside the NO analyzer due to reaction of 50 ppb initial NO (NO\textsubscript{i}) with O\textsubscript{3}. NO was introduced from a calibration cylinder, and O\textsubscript{3} was introduced from the output of the PAM reactor.

\begin{equation}
\ln \left( \frac{[\text{NO}]}{[\text{NO}\textsubscript{i}]} \right) = -0.0833 - 0.550 \cdot [\text{O}_3] \\
\end{equation}

\[ r^2 = 0.996 \]

Figure S2. Modeled steady-state (a) NO:HO\textsubscript{2}, and (b) OH:NO\textsubscript{3} as a function of input-[N\textsubscript{2}O] into the PAM oxidation flow reactor with mean residence time = 80 sec for: low, medium, and high I\textsubscript{254} = 0.032 × 10\textsuperscript{15}, 0.64 × 10\textsuperscript{15} and 6.4 × 10\textsuperscript{15} ph cm\textsuperscript{-2} sec, respectively, at fixed [H\textsubscript{2}O] = 1\% and [O\textsubscript{3}] = 5 ppm.
Figure S3. Modeled steady-state (a) NO, (b) NO:HO$_2$, and (c) OH:NO$_3$ as a function of input [N$_2$O] into the PAM oxidation flow reactor with mean residence time = 80 sec for: low, medium, and high [O$_3$] = 0.5, 5, and 50 ppm respectively, at fixed [H$_2$O] = 1% and I$_{254}$ = 6.4 x 10$^{15}$ ph cm$^{-2}$ sec.
Figure S4. Modeled steady-state (a) NO, (b) NO:HO₂, and (c) OH:NO₃ as a function of input [N₂O] in the PAM oxidation flow reactor with mean residence time = 80 sec for: low, medium, and high [H₂O] = 0.07, 1, and 2.3% respectively, at fixed [O₃] = 5 ppm and I₂54 = 6.4 × 10¹⁵ ph cm⁻² sec⁻¹.
Figure S5. Modeled steady-state (a) OH exposure, (b) [NO], (c) NO:HO$_2$, and (d) fractional oxidative loss to OH, NO, O$_3$, and NO$_3$ as a function of input [N$_2$O] corresponding to isoprene - OH oxidation conditions at low OH exposure in the PAM reactor. Error bars represent uncertainty in model outputs (Peng et al., 2015) and in accuracy of N$_2$O flow controller.
Figure S6. Modeled steady-state (a) OH exposure, (b) [NO], (c) NO:HO\textsubscript{2}, and (d) fractional oxidative loss to OH, NO\textsubscript{3}, O\textsubscript{3}, and NO\textsubscript{3} as a function of input [N\textsubscript{2}O] corresponding to isoprene + OH oxidation conditions at high OH exposure in the PAM reactor. Error bars represent uncertainty in model outputs (Peng et al., 2015) and in accuracy of N\textsubscript{2}O flow controller.
Figure S7. Modeled steady-state (a) OH exposure, (b) O_3 exposure, (c) [NO], (d) NO:HO_2, and (e) fractional oxidative loss to \( \text{OH}, \text{HO}_2, \text{O}_3, \text{NO}_2 \) as a function of input [N_2O] corresponding to isoprene + OH-\( \alpha \)-pinene oxidation conditions at low OH exposure in the PAM reactor. Error bars represent uncertainty in model outputs (Peng et al., 2015) and in accuracy of N_2O flow controller.