

Response to reviewers for the paper

We thank the anonymous referee and Prof. Nizkorodov for their comments on our manuscript. To guide the review process, we have copied the referee's comments in black text. Our responses are in blue text. We respond to Referee #1 and #2 comments, with alterations to the paper indicated in bold or struck through text below and in annotations to the revised manuscript.

Referee #1

General Comments

In this manuscript the authors present a new method for creating NO₃ radicals for atmospheric chemistry experiments by photolysis of aerated cerium ammonium nitrate solutions. The photolysis apparatus is described and the results of an evaluation of the effects of different experimental parameters on the modeled concentrations of species in solution and species in the gas phase based on mass spectrometer measurements is presented. The apparatus is also used to generate NO₃ radicals for a reaction with beta-pinene in an oxidation flow reactor (OFR) for comparison of mass spectra of gas- and particle-phase products with the literature.

The experiments and modeling were well done, and the results are thoroughly discussed and interpreted with an excellent use of information on this solution photochemistry obtained from the literature. This method has some advantages over those currently used to create NO₃ radicals and so may see considerable use by the atmospheric chemistry community. I think the manuscript is appropriate for publication after the following minor comments are addressed.

Specific Comments

1. Line 329–332: The IC₁₀H₁₆N₂O₇⁻ ion is a hydroxy dinitrate not a dinitrate, so it could not have been formed directly from an RO₂• + NO₃ → RONO₂ + O₂ reaction of the beta-nitrooxyperoxy radical. It would require a nitrooxyhydroxyperoxy radical, for which I am not aware of a formation pathway. Also, I did not find anywhere in the Orlando and Tyndall (2012) paper that suggests that nitrates can be formed by a RO₂• + NO₃ reaction, nor do any others I am aware of. The only reaction they describe is RO₂• + NO₃ → RO• + NO₂ + O₂. I suggest you just say you don't know how this product forms.

Revised text:

L329-L332: "The IC₁₀H₁₆N₂O₇⁻ **hydroxy dinitrate, which was obtained also previously observed in FIGAERO-CIMS spectra following reaction of the β-nitrooxyperoxy radical of α-pinene/NO or NO₃ SOA (Nah et al., 2016; Bates et al., 2022), was generated via an unknown reaction pathway. Because model calculated NO:NO₃ was the order of 10⁻⁵ under these conditions, its formation from the RO₂ + NO₃ reaction seems more likely (Orlando and Tyndall, 2012).**"

2. Line 367–369: Competing NO₃ and O₃ reactions are only a problem if one tries to synthesize NO₃ radicals online. It is not an issue when one synthesizes N₂O₅ and then stores it in a freezer until needed. The synthesis is simple and one can easily make enough in a couple hours to last for months or years.

Revised text:

L367-369: “Another advantage of Ce(IV) irradiation is that it does not involve the use of O₃ as a reagent, therefore eliminating the possibility of competing O₃ and NO₃ oxidation of compounds that are reactive towards both oxidants **if NO₂+O₃ reactions and/or online N₂O₅ synthesis are used as the NO₃ source** (Lambe et al., 2020).”

3. Since most people using this method would be interested in knowing what RO₂• reaction regime they are in, I suggest supplying a more detailed discussion of how the different synthesis conditions affect the relative concentrations of NO₃, NO₂, and HO₂ radicals, and noting that the rate constant for RO₂• + HO₂ is about 10x greater than for RO₂ + NO₃ or NO₂. It would be especially useful to say how to run the source if one wants to be in a RO₂• reaction regime dominated by reactions with HO₂, NO₂, or NO₃
4. How rapidly do gas-phase products collide with the walls in an OFR? If ROONO₂ products formed from RO₂• + NO₂ → ROONO₂ are significant with this method then the collisions will likely be a RO₂• radical sink and a source of R=O products via loss of HNO₃ from ROONO₂.

Because both comments consider the fate of RO₂, we combined our response. In a similar OFR to the one used here, Palm et al. (2016) estimated a first-order wall loss rate coefficient of 0.0025 s⁻¹ (τ_{wall} = 400 s) for condensable LVOC. As discussed in the revised text below, we anticipate that wall losses of alkyl RO₂ are negligible in the OFR because they thermally decompose within seconds. Acyl RO₂ species could be long-lived enough to interact with the walls, but we note that the calculated mean OFR residence time (τ_{OFR} = 120 s) is shorter than τ_{wall}, thus, we anticipate that wall losses are a minor sink for acyl RO₂.

Revised text:

L357: “Because C₁₀H₁₇NO₄ is formed from RO₂+RO₂ [...] differences in gas-phase C₁₀H₁₇NO₄ and C₁₀H₁₆N₂O₇ yields were likely related to differences in the relative rates of RO₂+RO₂ and RO₂ + NO₃ reaction pathways in the study by Takeuchi and Ng (2019) compared to this work.

To further investigate the fate of RO₂ generated from VOC + NO₃ reactions as a function of CAN irradiation conditions, we calculated the fractional oxidative loss of generic alkyl and acyl RO₂ species due to reaction with HO₂, NO₃ and NO₂ (F_{RO₂+HO₂}, F_{RO₂+NO₃}, F_{RO₂+NO₂}) using Equations 1-3:

$$F_{RO_2+HO_2} = k_{RO_2+HO_2}[HO_2]/(k_{RO_2+HO_2}[HO_2] + k_{RO_2+NO_3}[NO_3] + k_{RO_2+NO_2}[NO_2])$$

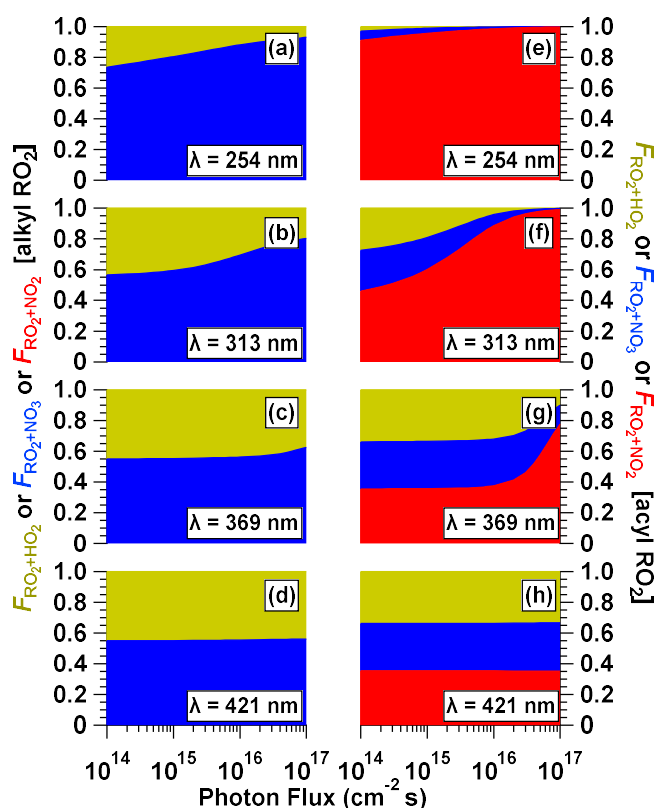
$$F_{RO_2+NO_3} = k_{RO_2+NO_3}[NO_3]/(k_{RO_2+HO_2}[HO_2] + k_{RO_2+NO_3}[NO_3] + k_{RO_2+NO_2}[NO_2])$$

$$F_{RO_2+NO_2} = k_{RO_2+NO_2}[NO_2]/(k_{RO_2+HO_2}[HO_2] + k_{RO_2+NO_3}[NO_3] + k_{RO_2+NO_2}[NO_2])$$

Here, $k_{RO_2+HO_2}$, $k_{RO_2+NO_3}$, and $k_{RO_2+NO_2}$ are reaction rate coefficients for the corresponding RO₂ + HO₂, RO₂ + NO₃ and RO₂ + NO₂ forward reactions whose values are summarized in Table S3. Several simplifying assumptions were made. First, we assumed that RO₂ + NO reactions were negligible. Second, we did not consider RO₂ isomerization/autooxidation and RO₂ + RO₂ reactions that are influenced by external factors. Third, we set F_{RO₂+NO₂} = 0 for alkyl-RO₂-generated RO₂NO₂, which thermally decompose on timescales of seconds or less (Orlando and Tyndall, 2012). Fourth, we assumed that vapor wall losses of acyl-RO₂-generated RO₂NO₂ were

a minor RO₂ sink because the OFR residence time ($\tau_{\text{OFR}} \approx 120$ s, Sect. 2.2) was significantly shorter than their estimated wall loss timescale ($\tau_{\text{wall}} \approx 400$ s; Palm et al. (2016)). Figure 10 shows calculated $F_{\text{RO}_2+\text{HO}_2}$, $F_{\text{RO}_2+\text{NO}_3}$ and $F_{\text{RO}_2+\text{NO}_2}$ values for alkyl-RO₂ and acyl-RO₂ as a function of photon flux over the range of NO₃ generation conditions presented in Fig. 6. For alkyl-RO₂, $F_{\text{RO}_2+\text{HO}_2}$ decreased and $F_{\text{RO}_2+\text{NO}_3}$ increased with increasing photon flux and decreasing irradiation wavelength. On the other hand, for acyl-RO₂, $F_{\text{RO}_2+\text{NO}_2}$ increased while $F_{\text{RO}_2+\text{HO}_2}$ and $F_{\text{RO}_2+\text{NO}_3}$ decreased over the same irradiation conditions. Overall, at the optimal NO₃ generation conditions (e.g. $\lambda = 369$ nm and $I_{369} \approx 10^{16}$ photons cm⁻² s⁻¹), our calculations suggest that $F_{\text{RO}_2+\text{HO}_2} \approx F_{\text{RO}_2+\text{NO}_3}$ for alkyl-RO₂ (Figs. 10c) and that $F_{\text{RO}_2+\text{HO}_2} \approx F_{\text{RO}_2+\text{NO}_3} \approx F_{\text{RO}_2+\text{NO}_2}$ for acyl-RO₂ (Fig. 10g).

We added the following figure to the revised manuscript:



We added the following citation to the revised manuscript:

B.B. Palm, P. Campuzano-Jost, A.M. Ortega, D.A. Day, L. Kaser, W. Jud, T. Karl, A. Hansel, J.F. Hunter, E.S. Cross, J.H. Kroll, A. Turnipseed, Z. Peng, W.H. Brune, and J.L. Jimenez. In situ secondary organic aerosol formation from ambient pine forest air using an oxidation flow reactor. *Atmospheric Chemistry and Physics*, Atmos. Chem. Phys., 16, 2943-2970, doi:10.5194/acp-16-2943-2016, 2016.

We added the following table to the revised supplement:

Table S3. Room-temperature bimolecular rate coefficients (k_{298}) used to calculate fates of alkyl and acyl organic peroxy radicals (alkyl-RO₂, acyl-RO₂) formed from VOC + NO₃ reactions as a function of CAN irradiation conditions summarized in Fig. 6. Kinetic data is adapted from Orlando and Tyndall (2012). Rate coefficients are given in units of cm³ molecule⁻¹ s⁻¹.

Reactant 1	Reactant 2	k_{298}
alkyl-RO ₂	HO ₂	7.7×10^{-12}
acyl-RO ₂	HO ₂	1.4×10^{-11}
alkyl-RO ₂	NO ₃	2.4×10^{-12}
acyl-RO ₂	NO ₃	3.2×10^{-12}
acyl-RO ₂	NO ₂	1.1×10^{-11}

Referee #2

I reviewed this paper to fill in for missing second review to avoid further delays in the open discussion process.

This is well written manuscript that proposes a new way of producing flows containing NO₃ for atmospheric experiments. The system is based on (complex) photochemistry of Ce(IV) nitrate, and the bulk of the manuscript describes tests in which concentrations, irradiation wavelengths, and light fluxes are varied to find the optimum setting for making NO₃. The system is then tested by making SOA from NO₃ produced by Ce(IV) nitrate and by conventional N₂O₅ thermal decomposition. I only have minor comments

CONTENT

1. I think section 3.5, especially the discussion of possible N₂O₆ formation, may distract the readers from the main message of the manuscript. This discussion is more pertinent to ionization chemistry in I- CIMS than to the topic of characterizing the NO₃ source. I would suggest shortening this section (or maybe even removing it and developing it into a stand-alone paper). But keeping it there is OK also, as I- CIMS is fairly common, and the discussion will be useful to I- CIMS users who work with this NO₃ source.

In our opinion some discussion of non-NO₃ photolysis products is useful because if nothing else it may help readers to improve experimental design, especially with regards to the presence/formation of HNO₂, HNO₃, HNO₄, and/or H₂O₂. With that said, we are receptive to your suggestion to shorten this section. We shortened the text in this section by ~50% by removing some text completely and moving the following text to the Supplement.

Section S1. Theoretical analysis of the gas-phase NO₃ + NO₃ → N₂O₆ reaction

We conducted a theoretical investigation of the gas-phase NO₃ + NO₃ → N₂O₆ reaction at T = 298 K and p = 1 atm. Quantum chemical calculations were performed using the Q-Chem 5.2 software package (Epifanovsky et al., 2021), and molecular geometries were obtained using the B3LYP density functional (Becke, 1993) and the 6-31G* basis set (Hariharan and Pople, 1973). All stationary points were refined by single point calculations applying the B3LYP density functional and the cc-pVTZ basis set (Dunning, 1989) as well as CCSD(T) (Jeziorski and Monkhorst, 1981) and the cc-pVTZ basis set. For NO₃ + NO₃ → N₂O₆, the calculated enthalpy of reaction (ΔH_{rxn}) was -35.8 kcal mol⁻¹ using the CCSD(T) method, and -21.9 kcal mol⁻¹ using the B3LYP method. By comparison, we calculated ΔH_{rxn} values of -26.5 (CCSD(T)) and -18.1 (B3LYP)

kcal mol⁻¹ for the NO₃ + NO₂ → N₂O₅ reaction; the corresponding energy change (ΔE_{rxn}) values agreed within 5% of previously obtained experimental and computational ΔE_{rxn} values for this reaction (Jitariu and Hirst, 2000; Glendening and Halpern, 2007). Thus, regardless of the quantum chemical method that was used, NO₃ + NO₃ → N₂O₆ appears to be an exothermic reaction, even more so than NO₃ + NO₂ → N₂O₅. While the reverse reaction N₂O₆ → 2 NO₃ is possible (although endothermic, as is N₂O₅ → NO₂ + NO₃) our analysis suggests that the thermodynamically favored reaction pathway is N₂O₆ → N₂O₄ + O₂, which had ΔH_{rxn} values ranging from -7.02 (CCSD(T)) to -6.15 (B3LYP) kcal mol⁻¹. By contrast, the reaction N₂O₆ → 2 NO₂ + O₂ had ΔH_{rxn} = 5.28 (CCSD(T)) and 5.58 (B3LYP) kcal mol⁻¹; however, because N₂O₄ → 2 NO₂ is fast (Poskrebyshev et al., 2001; Atkinson et al., 2004), the overall reaction N₂O₆ → 2 NO₂ + O₂ is the favored N₂O₆ removal pathway in the gas phase, and in solution may occur in addition to or instead of Reaction R4.

Section S2 Discussion of additional I⁻ CIMS signals

Section S2.1 IO_x⁻, NO₂⁻, NO₃⁻, IHNO₃⁻, HNO₃NO₃⁻, and IN₂O₇⁻

Figure S4 shows time series of I⁻, IH₂O⁻, IO⁻, IO₂⁻, NO₂⁻, NO₃⁻, IHNO₃⁻, and HNO₃NO₃⁻ obtained with the CIMS following irradiation of a mixture of 0.5 M CAN and 1.0 M NaNO₃. Signals of I⁻, IH₂O⁻ and IHNO₃⁻ decreased following irradiation of the CAN/NaNO₃ mixture, whereas IO⁻, IO₂⁻, NO₂⁻, NO₃⁻, and HNO₃NO₃⁻ increased. One potential source of IO_x⁻ is I⁻ + O₃ reactions in the CIMS IMR; if this reaction was the sole source of IO_x⁻ here, we estimate an upper limit O₃ mixing ratio of approximately 15 ppbv present in the IMR (Dörich et al., 2021). NO₂⁻ is generated following the reaction of I⁻ and/or IO_x⁻ with HNO₂ (Abida and Osthoff, 2011), and NO₃⁻ is generated from the reaction of I⁻ and/or IO_x⁻ with multiple nitrogen oxides, including NO₃, HNO₃, HNO₄, and N₂O₅ (Huey et al., 1995; Veres et al., 2015; Dörich et al., 2021). Figure S4 additionally shows a time series of IN₂O₇⁻, and Figures S5, S6, and S7 shows high-resolution CIMS spectra at m/Q = 235, 251, and 267. Given IN₂O₇⁻:IN₂O₅⁻ ≈ 10⁻³ coupled with similar IN₂O₅⁻ and IN₂O₇⁻ temporal profiles (Fig. S4), we hypothesize that N₂O₅ + IO_x⁻ reactions in the IMR were the primary source of IN₂O₇⁻.

Section S2.2 IN₂O₄⁻

IN₂O₄⁻ was not detected with the CIMS following irradiation of aqueous Ce(IV), presumably because its hydrolysis rate was too fast (Park and Lee, 1988). In an attempt to decrease the hydrolysis rate, separate experiments were conducted in which the effluent of 40 g of irradiated solid CAN was sampled with the CIMS. At the sample sizes that were used, the solid CAN contained enough solvated HNO₃ and/or H₂O that its irradiation provided sufficient production of nitrogen oxides for CIMS detection. As shown in Figures S8, S9 and S10, CIMS NO₂⁻, IN₂O₄⁻, I(HNO₂)_n⁻, and (HNO₂)_nNO₃⁻ signals were significantly higher following irradiation at λ = 254 nm than at the other wavelengths, and Fig. S11 confirms that IN₂O₄⁻ was the dominant ion signal at m/Q = 219. Taken together, these observations support our hypothesis that HNO₂ was generated following fast N₂O₄ hydrolysis in aqueous solution.

EDITORIAL

2. L82: I would mention that flux at 421 nm was not quantified

Revised text:

L82: “To quantify the photon flux *I* in the photoreactor for studies that used λ = 254, 313, or 369 nm radiation, we measured the rate of externally added O₃ (λ = 254 nm) or NO₂ photolysis (λ = 313 or 369

nm) as a function of lamp voltage under dry conditions (RH < 5%). **The photon flux was not quantified in studies that used $\lambda = 421$ nm radiation.**

3. L85, L170, etc.: I would suggest replacing “I-values” with a more explicit name

Revised text:

L82-L85: “To quantify the photon flux I_{λ} in the photoreactor for studies that used $\lambda = 254, 313, \text{ or } 369$ nm radiation, [...] formation. **Photon flux** values were then calculated...”

L169-L170: “These differences in $[\text{NO}_3]$ were larger than the differences in calibrated **photon flux** values at the maximum output of each lamp type ($\pm 40\%$; Sect. 2.1).”

L231: “[NO_3] values decreased at higher **photon flux** values due to conversion of NO_3 to NO_2 via photolysis.”

4. L94: Table S2 is referred to before Table S1 is mentioned on line 118. Probably best to fix the order.

Thank you. We have switched the order of Tables S1 and S2 in the supplement and the corresponding references in the text.

5. L102: do you have an estimate of the effect of RO_2 reactions, perhaps from OFR modelling?

Thank you for your question and suggestion. To investigate this, we constructed a simple kinetic model to calculate the mean RO_2 concentration generated from NO_3 oxidation of the VOC tracers in the OFR over 120 sec residence time. We assumed NO_3 oxidation of each VOC generated the same generic/lumped RO_2 and that this RO_2 reacted with NO_3 at a rate coefficient of $2.4 \cdot 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Table S3, see response to Comment #4 by Referee #1). The model was initialized using the VOC concentrations listed in Table S2 (now Table S1) and the initial NO_3 mixing ratio was varied between 1 and 1000 ppbv. We then calculated the external NO_3 reactivity of this lumped RO_2 species and normalized it to the total external NO_3 reactivity of the VOC tracers (5 s^{-1}). The result is shown below:

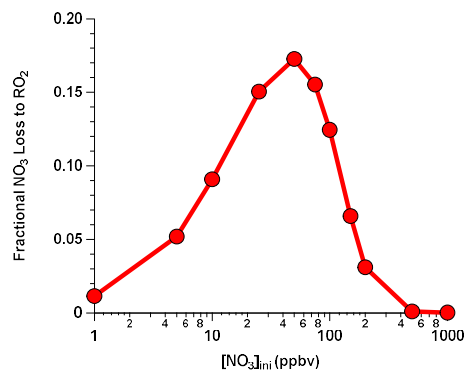


Figure S2. Fractional NO₃ consumption by RO₂ generated from VOC + NO₃ reactions during NO₃ characterization studies described in Sect. 3.1.

We interpret this result as follows: at the lowest [NO₃], less RO₂ is generated because less VOC is consumed by NO₃, whereas at the highest [NO₃], the VOC tracers (and RO₂) were consumed quickly enough that sustaining high RO₂ concentrations was more difficult. At an initial NO₃ mixing ratio of 50 ppbv, a maximum of ~17% of the NO₃ was consumed by RO₂.

Revised text:

L102: “Here, we assumed that the total concentration of reacted VOCs was equal to the concentration of NO₃ injected into the OFR. Because NO₃ may additionally react with organic peroxy radicals (RO₂) generated from VOC + NO₃ reactions as well as OVOCs, these calculated NO₃ concentrations represent lower limits. **Modeling calculations suggest that the fractional consumption of NO₃ by RO₂ ranged from <0.01 to 0.17 over the range of conditions that were studied (Fig. S2).**”

Figure S2 was added to the revised supplement.

- Figure 3: instead of saying “Additional figure notes” you can say “The black dot corresponds to data from Wine et al. (1988)”

Revised Figure 3 caption:

“Figure 3. (a) [NO₃] values obtained from irradiated CAN & 6.0 M HNO₃ and CAN & 4.8 M NaNO₃ mixtures as a function of irradiation wavelength. Results were normalized to [NO₃] achieved with irradiation of CAN/HNO₃ mixtures at λ = 369 nm or CAN/NaNO₃ mixtures at λ = 254 nm. Error bars represent ±1σ uncertainty in binned [NO₃] values. (b) Extinction cross sections (σ_{ext}) of CAN/HNO₃ and CAN/NaNO₃ mixtures (for details see Sect. 2.3). ~~Additional figure notes: 1~~ **The black dot corresponds to data from Wine et al. (1988).**”

- L216 and Figure 5: I presume the data are for 369 nm only. I would mention it here and in the figure caption.

The data for CAN/HNO₃ mixtures are for 369 nm only, but the data for CAN/NaNO₃ mixtures are for 254 nm. Revised text:

L216: “Figure 5 shows normalized $[\text{NO}_3]$ values obtained from UVA-light-irradiated mixtures of 0.5 M CAN & 6.0 M HNO_3 ($\lambda = 369 \text{ nm}$) and UVC-light-irradiated mixtures of 0.5 M CAN & 1.0 M NaNO_3 ($\lambda = 254 \text{ nm}$) as a function of photon flux ranging from 6.9×10^{14} to 7.5×10^{15} photons $\text{cm}^{-2} \text{ s}^{-1}$. Results for both CAN/ HNO_3 and CAN/ NaNO_3 mixtures were normalized to $[\text{NO}_3]$ achieved with 0.5 M CAN, 6.0 M HNO_3 and $I_{369} = 6.8 \times 10^{15}$ photons $\text{cm}^{-2} \text{ s}^{-1}$ ”

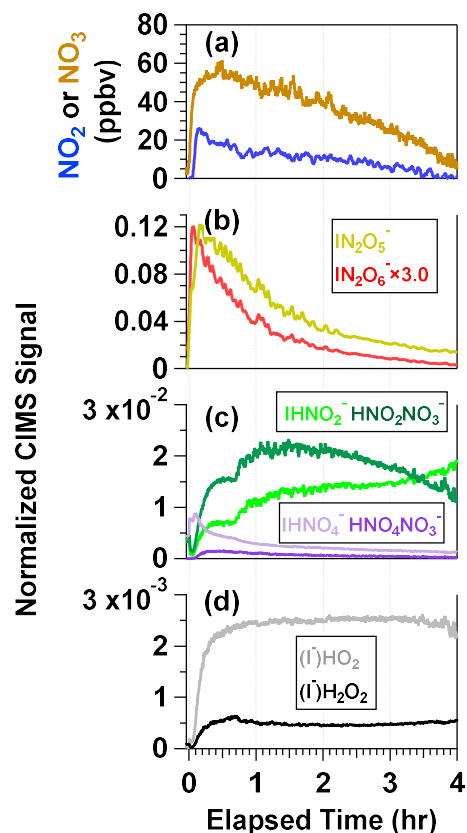
Figure 5 caption: “Normalized $[\text{NO}_3]$ values obtained from irradiated mixtures of 0.5 M CAN and 6.0 M HNO_3 ($\lambda = 369 \text{ nm}$) or 0.5 M CAN and 1.0 M NaNO_3 ($\lambda = 254 \text{ nm}$) as a function of photon flux ranging from 6.9×10^{14} to 7.5×10^{15} photons $\text{cm}^2 \text{ s}^{-1}$.”

8. Figure 7 caption: a $\text{NO}_2 \rightarrow$ (a) NO_2

Thank you – the correction has been made.

9. Figure 7: would it make sense to also include NO_3 mixing ratio in this figure measured under the same conditions, similar to the one in Figure 2?

Thank you for your suggestion. A revised version of Figure 7 is shown below:

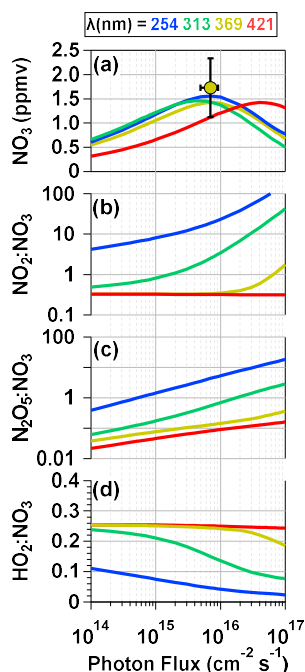


Revised Figure 7 caption: “Figure 7. Time series of (a) NO_2 and NO_3 (b) N_2O_5 and N_2O_6 ...”

The pertinent revised text in the first paragraph of the (revised) Section 3.5:

“Figure 7 shows time series of reactive nitrogen and reactive oxygen species detected following irradiation of a mixture of 0.5 M CAN and 1.0 M NaNO₃ ($I_{254} \approx 10^{16}$ photons cm⁻² s⁻¹) shown here because the signal-to-noise in CIMS measurements of irradiated CAN/NaNO₃ mixtures was generally better than in measurements of irradiated CAN/HNO₃ mixtures due to reagent ion depletion by HNO₃. **A time series of [NO₃] obtained from VOC tracer decay measurements in a separate experiment under similar irradiation conditions is also shown.** The NO₂ and NO₃ mixing ratios reached maximum values of 26 and 58 ppbv shortly after the lights were turned on (Fig. 7a), suggesting an initial NO₂:NO₃ \approx 0.45.”

Although it was not requested by the reviewer here, to facilitate comparison of measured and modeled NO₃ values in Figure 6, we also calculated the mean NO₃ mixing ratio over the first 4 hours of the experiment shown in Fig. 2 (59.3 ppbv) (to correspond to the 4 hour model simulation time (L132)) used to generate the results that are shown in Fig. 6). The revised Figure 6 is shown below:



Revised Figure 6 caption:

Figure 6. Model-calculated (a) [NO₃], (b) NO₂:NO₃, (c) HO₂:NO₃, and (d) N₂O₅:NO₃ values in solution as a function of photon flux ranging from 1×10¹⁴ to 1×10¹⁷ photons cm⁻² s⁻¹ following $\lambda = 254, 313, 369$ and 421 nm irradiation of a mixture containing 0.5 M CAN and 6.0 M HNO₃. **[NO₃] obtained from measurements shown in Fig. 2 is plotted in (a).** For details see Sect. 2.3 and Tab. S1.

Revised text:

L226: “To examine concentrations of NO₃ and a subset of additional gas-phase photolysis products obtained over a wider range of conditions, Figure 6 plots model-calculated [NO₃], NO₂:NO₃, HO₂:NO₃, and N₂O₅:NO₃ values as a function of photon flux ranging from 1×10¹⁴ to 1×10¹⁷ photons cm⁻² s⁻¹ following $\lambda = 254, 313, 369$ and 421 nm irradiation of a mixture of 0.5 M CAN and 6.0 M HNO₃. **Figure 6a also plots the measured [NO₃] obtained from irradiation of a mixture of 0.5 M CAN and 6.0 M HNO₃ at $I_{369} = 7 \times 10^{15}$ photons cm⁻² s⁻¹ (Fig. 2) after correcting for dilution between the photoreactor and the OFR (Sect. 2.2)**

and application of a NO_3 wall loss rate coefficient of 0.2 s^{-1} within the photoreactor (Dubé et al., 2006). At this photon flux value, the model-calculated $[\text{NO}_3] = 1.4 \text{ ppmv}$ agrees with $[\text{NO}_3] = 1.7 \pm 0.6 \text{ ppmv}$ obtained from measurements. When considering only the primary photochemical process (Reactions R1-R5), maximum $[\text{NO}_3]$ values within $\pm 10\%$ of each other were achieved at photon fluxes ranging from 5×10^{15} ($\lambda = 313 \text{ nm}$) to 4×10^{16} photons $\text{cm}^{-2} \text{ s}^{-1}$ ($\lambda = 421 \text{ nm}$).

The following citation was added to References:

Dubé, W. P., Brown, S. S., Osthoff, H. D., Nunley, M. R., Ciciora, S. J., Paris, M. W., McLaughlin, R. J., and Ravishankara, A. R.: Aircraft instrument for simultaneous, in situ measurement of NO_3 and N_2O_5 via pulsed cavity ring-down spectroscopy, *Rev. Sci.*, 77, 34–101, <https://doi.org/10.1063/1.2176058>, 2006.

10. L330: was the order -> was of the order

Revised text: L330: “Because model-calculated $\text{NO}:\text{NO}_3$ was on the order of 10^{-5} under these conditions...”

11. Figure S2: captions mentions acetonitrile but it is not clear what role it plays in the data as normalization is done with respect to thiophene. Was everything first normalized to acetonitrile as the text states? I would mention this in the caption more explicitly.

That is correct – to clarify, we paraphrased the text from L145-L147 in the revised Figure S2 caption.

Revised text:

Figure S2. “Relative rate coefficients obtained from Vocus measurements of acetonitrile ($\text{C}_2\text{H}_3\text{N}$), thiophene ($\text{C}_4\text{H}_4\text{S}$), 2,3-dibenzofuran ($\text{C}_8\text{H}_8\text{O}$), and cis-3-hexynyl-acetate ($\text{C}_8\text{H}_{14}\text{O}_2$) tracers used in characterization studies described in Sect. 3.2. **Here, concentrations of $\text{C}_4\text{H}_4\text{S}$, $\text{C}_8\text{H}_8\text{O}$, and $\text{C}_8\text{H}_{14}\text{O}_2$ were first normalized to the $\text{C}_2\text{H}_3\text{N}$ concentration to correct for changes in the syringe pump output over time and then normalized to the VOC concentration prior to NO_3 exposure.** Literature relative rate coefficients obtained from kinetic data published by Atkinson (1991) and Atkinson et al. (1995).”

12. Table S1: It appears the authors list absorption cross section (or perhaps a product of that with the quantum yield) instead of the photolysis rate constants for photolysis processes. I would note this to avoid confusion.

We fixed a typo in the Table S1 caption by changing the units of the noted absorption cross sections (cm^{-2} to cm^2) and added some clarification text:

Table S1: “KinSim mechanism used to calculate concentrations of species associated with irradiation of CAN/HNO_3 mixtures. Rate coefficients (**blue text, red text or black text**) or absorption cross sections (**teal text**) are given in units of $\text{cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ (**blue text**), $\text{M}^{-1} \text{ s}^{-1}$ (**red text**), cm^2 (**teal text**), or s^{-1} (**black text**).”

13. Table S1: when multiple values for the same process are listed, such as the Martin and Stevens (1978) values for $\text{Ce(III)} + \text{NO}_3$ reaction, which one is being used in the model?

For results presented in the main paper, we used values corresponding to the 6.0 M HNO₃ case. The other values correspond to 1.0 M and 3.0 M HNO₃ solutions, indicated by subscripts defined in the last line of the Table S1 caption: “Additional table notes: ¹[HNO₃]=1.0 M, ²[HNO₃]=3.0 M, ³[HNO₃]=6.0 M” and referenced in the “Citation” column of the table. This notation was chosen mainly for brevity to allow the table to fit on the page. To make the notation more intuitive, we additionally color-coded the applicable values in the “Citation” column of this table.

Revised text in the last sentence of table caption:

“Citations of rate coefficient and absorption cross section values that are specifically applicable to mixtures containing [HNO₃] = 1.0 M, 3.0 M or 6.0 M are colored with brown, violet, or orange text, respectively.”

Revised table:

Reactant 1	Reactant 2	Product 1	Product 2	Product 3	RateCoeff	Citation
Ce ^{IV} NO ₃	hν ₂₅₄	[Ce ^{III} ...NO ₃] ⁺	NO ₃		2.7E-17	this work
					3.1E-17	this work
					3.1E-17	this work
Ce ^{IV} NO ₃	hν ₂₁₃	[Ce ^{III} ...NO ₃] ⁺	NO ₃		3.1E-17	this work
					3.5E-17	this work
					4.5E-17	this work
Ce ^{IV} NO ₃	hν ₉₆₉	[Ce ^{III} ...NO ₃] ⁺	NO ₃		8.7E-18	this work
					1.2E-17	this work
					2.5E-17	this work
Ce ^{IV} NO ₃	hν ₄₂₁	[Ce ^{III} ...NO ₃] ⁺	NO ₃		1.0E-18	this work
					1.5E-18	this work
					4.4E-18	this work
[Ce ^{III} ...NO ₃] ⁺		Ce ^{IV} NO ₃ ⁻			5.12E+04	Martin and Stevens (1978)
					6.30E+03	Martin and Stevens (1978)
[Ce ^{III} ...NO ₃] ⁺		Ce ^{III}	NO ₃		0	Martin and Stevens (1978)
					4.36E+04	Martin and Stevens (1978)
					6.76E+04	Martin and Stevens (1978)
Ce ^{III}	NO ₃	Ce ^{IV} NO ₃ ⁻			7.74E+04	Martin and Stevens (1978)
					6.00E+07 (9.96E-14)	Martin and Stevens (1978)
					1.08E+06 (1.79E-15)	Martin and Stevens (1978)
					1.78E+06 (2.96E-15)	Martin and Stevens (1978)