Response to reviewers for the paper "HO_x and NO_x production in oxidation flow reactors via photolysis of isopropyl nitrite, isopropyl nitrite-d_7, and 1,3-propyl dinitrite at λ = 254, 350, and 369 nm."

We thank the reviewers for their comments on our paper. To guide the review process we have copied the reviewer comments in black text. Our responses are in regular blue font. We have responded to all the referee comments and made alterations to our paper (**in bold text**).

Anonymous Referee #1

The author developed a new method using alkyl nitrite photolysis as a source of OH radical and NOx. Kinetic modeling was done to support that a much wider range of NO:HO2 ratio (10 -10000) was achieved. They present experimental and model characterization of the OH exposure and NOx levels generated via photolysis of C3 alkyl nitrites in the Potential Aerosol Mass (PAM) OFR. Together with chemical ionization mass spectrometer measurements of multifunctional oxidation, the author compared the products α-pinene generated following the exposure of to HOx and NOx obtained using both isopropyl nitrite and O3 + H2O + N2O methods. This new method proposed by Lambe et al. would open the prospect of OFR experiments at high NO. The paper is well written and organized. Few issues need to be addressed.

R1.1) While the author uses alkyl nitrates as a source of HOx and NOx in the oxidation flow reactor, their method provides a wider range of NO:HO2 ratio and lower OH exposure. The chemical ionization mass spectrometer measurements of α-pinene oxidation products from different alkyl nitrates experiments are somehow comparable to some ambient measurement. While this method sounds promising, I would also be glad to know any disadvantage of using this method as it is important for the oxidation flow reactor users to avoid unwanted chemical reactions. For example, by photolysis of alkyl nitrate, we will generate a lot of RO, RO2 and R radicals. These radicals may also involve in the further reactions with intermediates from the oxidation of injected VOCs. Therefore produce additional products other than only from the oxidation of injected VOCs. I wonder if the author observes any such kind of products in their mass spectra data? Is this process significant?

We modified the text as follows:

P12, L18-26: "Taken together, OFR254/**OFR**185-iN_2O and OFR369-i(iPrONO/iPrONO-d_7) are complementary methods that provide additional flexibility for NO_x-dependent OFR studies. **OFR254/OFR185-iN_2O generate variable-NO_x photooxidation conditions (NO:HO2≈0 - 100), and are suitable for the characterization of multigenerational oxidative aging processes at up to OH_{exp} ~ (5-10)*10^{11} molecules cm^{-3} s (~5-10 eq. days).** OFR369-i(iPrONO)/OFR369-i(iPrONO-d_7) generate high-NO photooxidation conditions (NO:HO_2≈10 - 10000) with minimal O_3 and NO_3 formation at longer photolysis wavelength than OFR254/185-iN_2O. We anticipate that alkyl nitrite photolysis is **advantageous** for the characterization of first-generation, high-NO_x photooxidation products of most precursors **at up to OH_{exp} ~ 1*10^{11} molecules cm^{-3} s (1 eq. day), which is comparable to environmental chambers investigating high-NO_x conditions.** The generation of OD (rather than OH) via OFR369-i(iPrONO-d_7) may be useful in photooxidation studies of unsaturated precursors due to the shift on the m/z of the addition products, though at the potential expense of generating more complex distributions of oxidation products. **Potential disadvantages of using alkyl nitrite photolysis as a HO_x source are: (1) restriction to high-NO photochemical conditions; (2) restriction to OH_{exp} of 1 eq. day or less; (3) additional complexity involved with integration of the alkyl nitrite source (compared to O_3 + H_2O + N_2O); (4) potential inability to retrofit a specific OFR design with blacklights; (5) it acts as an interference that precludes NOx measurements by chemiluminescence detection.**

In regards to the reviewer's comment about R, RO, and RO2 radicals produced from isopropyl nitrite photolysis, the species that are treated in our model (R5-R17) include:

R: CH_3
RO: i-C_3H_7O, CH_3CO, HCO
RO2: CH_3O_2, $CH_3C(O)O_2$

Of the above species, in the presence of oxygen -- typically the case in most modern OFR studies -- all of the R and RO species (CH_3, i-C_3H_7O, CH_3CO, and HCO) are too short-lived to directly participate in reactions with RO_2 radicals formed from the oxidation of injected VOCs:

- CH_3 + O_2 generates CH_3O_2
- i-C_3H_7O + O_2 mostly generates HO_2 and acetone
- CH_3CO + O_2 generates $CH_3C(O)O_2$
- HCO + O_2 generates CO + HO_2

Thus, the most potentially problematic species include CH_3O_2 and $CH_3C(O)O_2$, which could participate in reactions with organic peroxy radicals generated from photooxidation of injected VOCs. Because generation of CH_3O_2 and $CH_3C(O)O_2$ only proceeds via iPrONO + hv → CH_3CHO + CH_3• + NO (R6), which has an estimated quantum yield of ~0.04 (P6, L16), the relative importance of these reactions is likely minor.

We modified the text as follows:

P6, L15-L16: "We assumed the quantum yield of Reaction R5 to be 0.5 **above 350 nm** (Raff and Finlayson-Pitts, 2010). **We assumed the quantum yield** of Reaction R6 to be 0.04 above 350 nm (value for t-butyl nitrite) (Calvert and Pitts, 1966), **suggesting minimal influence of CH_3O_2 and $CH_3C(O)O_2$ under these conditions that are generated via Reactions R7, R10, and R11 following iPrONO decomposition to CH_3 and CH_3CHO via Reaction R6. At 254 nm, the influence of CH_3O_2 and $CH_3C(O)O_2$ on ensuing photochemistry may be more significant. This is due to a higher quantum yield of Reaction R6 at 254 nm, which is estimated to be 0.86 under vacuum (Calvert and Pitts, 1966).**"

R1.2) P1 Line 4: Delete "t" before "λ = 254 nm"

Deleted.

R1.3) P3 Line 18-22: The author tried to use a NOx analyzer (Model 405 nm, 2B Technologies) to quantify the NO/NO2 mixing ratio. As shown in Figure S1 (b), the alkyl nitrates also show absorption at 405 nm which is the working wavelength of the NOx analyzer. Though the absorption cross section of alkyl nitrates is about one order of magnitude lower than that of the NO2, the mixing ratio of alkyl nitrates can be much higher than NO2, thus bias the NO2 and NO measurement. To perform the measurement, the author needs to correct the absorption by the alkyl nitrates.

Please see the text on P3, L23, where we stated that "we constrained [NO] and [NO_2] using the photochemical model discussed in Section 2.4" because we had difficulty correcting for absorption by the alkyl nitrites.

R1.4) P4 Line 20-24: To test this hypothesize, the author can simply measure the emission spectra of the UV lamps. This measurement can provide a direct proof to see the influence of longer wavelengths emission lines.

This is a fair point. We did not have access to an instrument that could measure the emission spectra of the 254 nm UV lamps; in the end, because OFR254-i(iPrONO) is not recommended, we did not pursue it further.

R1.5): A recent study by Ye et al. 2018 (ACP) found under wet conditions, heterogeneous uptake of SO2 onto organic aerosol was found to be the dominant sink of SO2, likely owing to reactions between SO2 and organic peroxides. This SO2 loss mechanism may bias the OH exposure measurement.

Thank you for the reference. In this work, OH exposure measurements were not conducted in the presence of organic aerosol (no VOCs were injected aside from alkyl nitrites, which themselves do not generate aerosol). Therefore we think that this is not an issue that is relevant to our results. However, we added the following sentence to the end of Section 2.2.2 to alert readers of the potential effect:

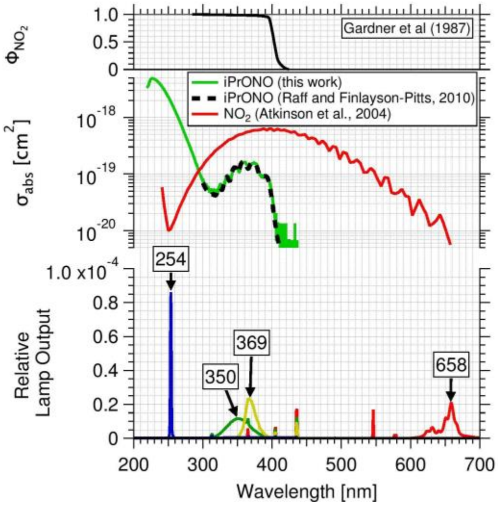
"While not applicable in this work, we note that heterogeneous uptake of SO_2 onto organic aerosol may bias OH exposure measurements (Ye et al., 2018)."

We added the following citation to references:

Ye, J., Abbatt, J. P. D., and Chan, A. W. H.: Novel pathway of SO_2 oxidation in the atmosphere: reactions with monoterpene ozonolysis intermediates and secondary organic aerosol, Atmos. Chem. Phys., 18, 5549-5565, https://doi.org/10.5194/acp-18-5549-2018, 2018.

R1.6) P6 Line 23-24: I suggest the author add the reference data into that plot to show directly that their results are in good agreement with literature data.

We added isopropyl nitrite absorption cross sections obtained from λ = 300 to 450 nm by Raff and Finlayson-Pitts (2010) (black dashed line) to a revised Figure S1 shown below:



R1.7) P8 Line 6: Add "The model results showed that" before "For [iPrONO] ≤ 5 ppm".

We modified the text as follows:

P8, L6: "Figure 3 shows measured and modeled OH_{exp} and NOx concentrations obtained from photolysis of 0.5 to 20 ppm iPrONO [...] **The model results showed that for** [iPrONO] ≤5 ppm, OH_{exp} increased with increasing [iPrONO] because the rate of OH production increased faster than the rate of OH destruction from reaction with iPrONO and NO_2. For [iPrONO] > 5 ppm, the opposite was true and OH_{exp} plateaued or decreased. A maximum OH_{exp} =7.8×10^{10} molecules cm^{-3} s was achieved via photolysis of 10ppm iPrONO, with corresponding modeled [NO] and [NO_2] values of 148 and 405 ppb respectively."

R1.8) P11 Line 28-29: How much can NO3 radical be produced in the OFR? If this is already included in the model, the author could show the results to indicate how important of NO3 radical oxidation.

The maximum NO_3 concentration in the model cases in this study is only ~1 ppt, since there is no O_3 in OFR-i(iPrONO) and the second step of the $NO_2 \rightarrow HNO_3 \rightarrow NO_3$ oxidation chain by OH is slow. We thus do not report the negligible NO_3 concentrations in the figures but added the following sentence at the end of Section 3.2:

"Modeled NO_3 concentrations were negligible in OFR-i(iPrONO) (<~1 ppt) because there is no O_3 present and NO_3 production via NO_2 + OH →HNO_3 and HNO_3 + OH →NO_3 + H_2O reactions was small."