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 #3

Summary and Recommendation

Authors introduce a new method for investigating NOx-dependent SOA formation pathways in oxidation flow reactors (OFRs). The new method uses alkyl nitrite photolysis to generate OH and NO2 with two different lights (254 nm and 369 nm). It is an improvement over previous methods used to study NOx-dependent SOA formation pathways in OFRs for three primary reasons. First, because it does not require extremely high levels of ozone and it does not produce nitrate radical as a by-product; both ozone and nitrate radical also contribute to oxidation of SOA precursors and their presence in the reactor creates major challenges for deconvolving contributions from the different oxidants. Second, it can be run with 369 nm lamps and avoid photolytic losses of SOA precursors that can occur with the more commonly used 254 nm lamps. Third, unlike batch reaction chamber studies which can only probe over timescales of hours to ~1 day, the OFR can be used to probe oxidative aging equivalent to multiple days. There were a number of challenges using the new method. First, the alkyl nitrites presented an interference in the NOx analyzer, and they had to use a photochemical model to estimate NOx in lieu of a direct measurement. Second, the NOx generated from alkyl nitrite photolysis introduced an interference in the SO2 analyzer and made it difficult to determine OH exposure. They corrected for this by performing an offline calibration relating SO2 decay and particulate sulfate to OH exposure.The technique does not achieve equivalent OH exposures longer than one day, but does appear to be a promising technique for OFR users to study high NOx SOA chemistry. This is particularly true for oxidation conditions using 369 nm lights. I recommend the manuscript for publication after the following comments are addressed.

R3.1) Elaborate on alkyl nitrite interference with NOx analyzer. Text says they attempted to correct for the interference "to no avail" (p.3, l. 22). What was the issue that prevented this correction?

Please see our response to similar R2.13.

R3.2) OH exposure calibration: not entirely clear how this calibration provided a measure of equivalent OH exposure from OH and NO2 generated from alkyl nitrites. It could be cleared up by better describing the link between Figure S4 and Figure¶ S5. The connection is lost by lack of clarity regarding the x-axis in Figure S4 and explicitly stating at the end of the paragraph how the relationship in Figure S5 is used to estimate OH exposure as presented in Figure S4. In Figure

S4, does the x-axis “sulfate” refers to both SO2 decay in the gas-phase and sulfate measured in the particles with the ACSM? There is something missing in the description that connects how the researchers propose to then presumably use the ACSM sulfate measurement in the presence of alkyl nitrites to estimate initial SO2 (Figure S5) and then relate that back to OH exposure using the relationship shown in Figure S4.

Please see our response to similar R2.3b, including the revised Figure S4 which we are hopeful will provide the necessary clarification to the question raised by Reviewer 3 here.

R3.3) Section 2.4: Additional reactions included in the model and all input parameters, rate constants, etc. are stated very clearly. Thank you. Uncertainties for actinic flux and organic nitrite concentration were also discussed very clearly. This model is being used to estimate NO and NO2 because of the NOx analyzer interference from alkyl nitrites (Section 2.2). I did not see an estimate of the uncertainty for NO and NO2 estimates. Please add those.

Section 2.4 listed estimates of uncertainties for the model inputs: pressure, temperature, [iPrONO], mean residence time, actinic flux, and absorption cross sections and bimolecular rate constants. Because the NO and NO_2 mixing ratios are model outputs, the propagated model uncertainties in model input parameters that influence [NO] and [NO_2] for the specific model scenarios are represented by the shaded regions in Figures 2 and 3.

R3.4) Figure 2: The explanation for lower OHexp values with 254 nm lights versus 350 nm and 369 nm was not very clear (page 7-8). In particular, elaborate on the concept, “Because σiPrONO;369 « σiPrONO;254 (Table 1), the effect of photolysis wavelength on [NO2] is proportional to σiPrONO, as expected” and how that relates to reduced OH exposure at 254 nm. The other explanation for reduced OHexp with 254 nm lights (decomposition of iC3H7O radical) is described in adequate detail, but it would help to better clarify the proportion of iPrONO that decomposes at this wavelength to provide more context for how significant this pathway is at the shorter wavelengths.

We attempted to clarify this point by modifying the text as shown in our response to reviewer comment R2.4.

R3.5) Section 3.4: OHexp and NO2 estimation equations If this section is going to be included in the main text of the results, the Figure S7 should also be included in the main text since that figure summarizes the main results from this section. Alternatively, the entire section could be moved to supplement. Can you clarify the significance of the results from this section somewhere in the text?

We moved Figure S7 to the main text of the revised manuscript. We modified the text as follows:

P9, L28: “Previous studies reported empirical OH_{exp} algebraic estimation equations for OFR185 and OFR254 (Li et al., 2015; Peng et al., 2015). **These equations parameterize OH_{exp} as a function of readily-measured experimental conditions, therefore providing a simpler**

alternative to detailed photochemical models that aids in experimental planning and analysis."

R3.6) One of the goals was to identify the optimal range of conditions for using the new alkyl nitrite method. Can you state the recommended "optimal" conditions more clearly AND also put the OFR conditions within that range into context relative to atmospheric conditions, particularly for NO:NO2 ratios and RO2:HOx? Are there certain conditions that should particularly be avoided? Can you make those more clear as well?

We modified the text as follows:

P12, L16: "Here, we adapted alkyl nitrite photolysis for new OFR applications by characterizing the photolysis wavelength, nitrite concentration, and nitrite composition that result in optimal HOx and NOx generation capabilities. **Based on our results, we recommend photolysis of 5-10 ppm alkyl nitrite at λ ~ 365-370 nm photolysis wavelength and >10^{15} photons cm^{-2} s^{-1} actinic flux. If the user has the resources to synthesize iPrONO-d_7, better performance is expected relative to iPrONO. Alkyl nitrite photolysis at λ = 254 nm is not recommended.** Taken together, OFR254/185-iN_2O and OFR369-i(iPrONO/iPrONO-d_7) are complementary methods that provide additional flexibility for NOx-dependent OFR studies. OFR369-i(iPrONO)/OFR369-i(iPrONO-d_7) generate high-NO_x photooxidation conditions (NO:HO_2 ≈10-10000; **NO:NO_2 ≈ 0.2-0.7)."**

R3.7) One of the stated benefits of OFRs in the intro is their ability to simulate "multiple days of equivalent atmospheric exposure." (P. 2, L. 4). Looking at Figures 2-4, it does not appear the OFR was capable of obtaining more than 1 day equivalent OH exposure either using the alkyl nitrite technique. Can you comment on how this timescale compares with smog chamber experiments investigating similar NOx pathways?

We note that the text on P2, L4 (which is part of the introduction) refers to other versions of the OFR chemistry described in previous publications.

Otherwise, one of the goals of this work was to achieve HOx generation via photolysis of 1,1,1,3,3,3-hexafluoroisopropyl nitrite (HFiPrONO) because modeling suggested it is capable of simulating multiple days of OH exposure due to its extremely low OH reactivity. This detail was omitted from the discussions manuscript but we have added it to the revised manuscript to provide additional context. As described in the paper, we were unable to synthesize HFiPrONO, following literature methods.

We modified the text as follows:

P9, L15: "We **predict** that OFR369-i(HFiPrONO) should attain higher OH_{exp} than OFR369-i(iPrONO) and OFR369-i(iPrONO-d_7) due to similar photolysis rates (Andersen et al., 2003) and ~200 times lower OH reactivity of HFiPrONO/hexafluoroacetone relative to iPrONO/acetone (Atkinson et al., 1992; Tokuhashi et al., 1999). **Simple modeling calculations suggest that application of OFR369-i(HFiPrONO) may achieve up to a week of equivalent OH exposure."**

P12, L21: “We anticipate that alkyl nitrite photolysis is suitable for the characterization of first-generation, high-NOx photooxidation products of most precursors, **at OH_{exp} comparable to environmental chambers investigating high-NO_x conditions.**”

R3.8) It would be helpful to see a direct comparison between OH exposure using the alkyl nitrite method versus other techniques that have been used to probe the high NOx pathway (for example, N2O addition).

We modified the text as shown in our response to the similar reviewer comment R1.1.

R3.9)P. 2, L. 28-30: alkyl nitrite were stored in amber vials and refrigerated until use. Can you clarify how long they can be stored and approximately how much time passed from synthesis to experimental use in these experiments?

We consulted with Pfaltz and Bauer, Inc., the company from which we obtained isopropyl nitrite. We received the following email response from a sales manager on 29 October 2018:

“Andy,

Per your request for the shelf life of our I10550, 2 years is a general guide.

We have seen 3 years if refrigerated and the container kept tightly closed away from moisture.

Regards,

Bob Milburn
Inside Sales Manager
Pfaltz & Bauer, Inc.
172 E. Aurora St.
Waterbury, CT 06708
tel 203-574-0075 X102
fax 203-574-3181
bobm@pfaltzandbauer.com
www.pfaltzandbauer.com”

We modified the text as follows:

“The resulting clear yellow liquid was dried over sodium sulfate, neutralized with excess sodium bicarbonate, and then stored in amber vials and refrigerated at 4°C until use **(within one week of synthesis in this work)**. **Under these storage conditions, the nominal shelf life of isopropyl nitrite and similar organic nitrites is approximately 2 years (B. Milburn, personal communication, 29 October 2018).**”