Review of Lambe et al. (2018)

Summary and overall review: This manuscript evaluates the use of alkyl nitrite (AN) photolysis as an OH-precursor in an oxidation flow reactor (OFR). Experimental and model simulation approaches are used to constrain the parameters of interest to OFR studies such as the actinic flux calibration, amount of OH and NO$_x$ generation for different types of ANs as precursors. Empirical calibration equations are fit to observed data to create a domain of different OFR operational parameters such as residence time, external reactivity, etc. within which future AN-OFR experiments may operate. Finally, using chemical ionization mass spectrometry, it is shown that molecular structures of $\alpha$-pinene SOA formed in the AN-OFR bear resemblance to that of ambient SOA previously observed in terpene-rich environments.

The manuscript is topically relevant to AMT and builds on the body of literature regarding OFRs. However there are several shortcomings in the experimental description, outlined in my comments below, that must be addressed before it is ready for publication.

Major comment(s):

1. The manuscript would benefit from a clearer description of the conditions when a PAM/OFR user would want to deploy nitrite as the OH precursor instead of using OFR185, OFR254, or injecting HONO. This manuscript demonstrates that AN can be used as a HOx precursor, but putting this method into better context with existing OFR practices would improve the manuscript.

2. OH estimation from SO$_2$ and sulfate: What collection efficiency was assumed for sulfate particles in the ACSM? An example of the sulfur mass balance should be shown (e.g., SO$_2$ inlet, SO$_2$ that survives the OFR, particulate SO$_4$, SO$_2$ lost to walls or other surfaces), at least in the SI.

3. OH$_{exp}$ estimation in Section 2.2.2: This work achieves $< 1$ day of OH$_{exp}$ and thus the uncertainties with estimating OH$_{exp}$ warrant more attention. One of the earlier OFR studies by Lambe et al. (2011) accounted for the influence of humidity on the growth of H$_2$SO$_4$ particles upon SO$_2$ oxidation in the OFR. This section describes how calibration of OH$_{exp}$ v. particulate sulfate (from conventional OFR-254 method, hence in presence of humidity) was applied to measured particulate sulfate (from iPrONO photolysis, presumably also with humidity) to estimate OH$_{exp}$.
   - It would be beneficial to briefly discuss how humidity was controlled in both these experiments and whether or not it was accounted for in correction of ACSM-measured sulfate mass (unless sample was dried prior to ACSM sampling, in which case that should be specified).
   - It is not surprising that the sulfate mass responded linearly to increasing [SO$_2$,0] in both these systems. The purpose of doing this inter-comparison was to see how much mass is formed in the iPrONO system v. in the conventional OFR-254 system, which would then imply how much OH$_{exp}$ is achieved in these two systems. Unless I am missing something, this comparison is not (but should be) plotted in Figure S5.

4. Page 6, L18-19: How were the reductions in quantum yields for R6 and R5 determined? This seems like a critical assumption in the modeling and it is not explained in much detail. What is the sensitivity of the model predictions to these quantum yields?
5. The presentation of the equations in Page 10 needs to be improved. First, there seems to be a formatting issue – the first equation appears as equations 3-6 and the second as equations 7-9. Each equation should have one number. Second, I don’t understand where these equations came from. Where are the data these equations are fit to (it should at least be shown in the SI)? What is the quality of the fit? How was the functional form determined?

6. Section 3.5: The comparison between the OFR and ambient CIMS spectra are presented only as in-line text. This comparison would be more effective if done graphically.

7. Relevance of this study for “Mimicking polluted atmospheric conditions”: the manuscript addresses a key limitation of the N₂O-OFR, in which, achieving < 1 equivalent day of NOₓ-dependent SOA formation is challenging. While the use of ANs as OH (or OD) precursors is shown to be promising for achieving such low oxidative exposures in this study, this potentially makes OH suppression a major concern for in-situ deployment of the AN-OFR (Peng et al. 2015). The chemical composition of α-pinene SOA formed in the AN-OFR (this study) bears resemblance to SOA previously observed in terpene-rich conditions in Centerville, Alabama and Hyytiälä, Finland (Yan et al., 2016; Massoli et al., 2018), suggesting that OH suppression may not be an issue. However, the manuscript lacks description of how much α-pinene was injected into the OFR, whether OH suppression was a competing influence, and if yes, whether or not it was accounted for.

Minor comments:

- Abstract line 3: extra “t” before λ.
- Equation 1: I assume that density is for the liquid, but please specify.
- P1 L17: space needed before (Mao et al., 2009…). This error repeats several times in citations throughout the manuscript.
- P2 L13: in the presence of humidified air (if I am understanding the reactions correctly).
- Page 3, L14: the light manufacturer LCD Lighting is listed in this line but not the previous lines.
- P3 L18-23: Is it possible to include some numbers describing this interference (maybe in the SI)? How was the conclusion of “no avail” drawn? Did the 2B monitor read increasing [NOₓ] with increasing [iPrONO] injection into dark OFR? Since this AN photolysis is a unique aspect of this manuscript, I think instrumental caveats should be better described.
- Somewhere in the methods section, the authors should mention what was the flow through the OFR in the calibration experiments. The flow rate through OFR for CIMS experiments is mentioned later, but the flow rate in non-CIMS experiments is not mentioned anywhere.
- P8 L5: this sentence is confusing, because it suggests that measured values of NOₓ are shown in Figure 3, while in fact they are not. Should be reworded accordingly.
- P8 L30 (and Figure 4): the explanation of higher NOₓ offsetting OH production efficiency seems straightforward enough that it should be reproduced by KinSim. However, it seems the model was not run (or not plotted in Figure 4) for this OFR369-i(1,3-Pr(ONO)₂) scenario. Can this be explained?
- Again, the caption for Figure 4 is confusing because “measured and modeled values … of (iPrONO-d7) and (1,3-Pr(ONO)₂)” suggests that the modeled values for BOTH these precursors are plotted, while in fact the model was apparently not run for the latter precursor (this goes back to my previous comment).
• Sections 3.3.1 and 3.3.2: are these sub-sections relevant to their parent section 3.3? The parent section title only mentions (iPrONO-d7) and (1,3-Pr(ONO)₂). In fact, are these subsections even important enough to be placed in this part of the manuscript? There was no prior discussion of why MeONO and HFiPrONO are important OH precursors. These sub-sections abruptly build up the importance of these two precursors, and then rapidly declare that they are not suitable precursors in the OFR. The narrative flows smoother going directly from experimentally measuring OH$_{exp}$ to setting up estimation equations i.e., from P8 L33 directly to P9 L27. I suggest moving 3.3.1 and 3.3.2 to the end of the manuscript or to the SI.

• Sections 3.2 and 3.3 are really hitting the same hammer (how much OH$_{exp}$ is generated from precursor $X$) on different nails ($X$ = iPrONO, deuterated iPrONO, etc.). I don’t see why they need to be separate sections.

• Figure S7b is missing a 1:1 line.

• P10 L18: NO2 needs a subscript.

• P11 L5: OFR operation details (flow rate, etc.) should be described in the Section 2.3. Also, amount of $\alpha$-pinene injected into OFR should be mentioned to give a sense of the OHR.

• P11 L11: compound nomenclature is missing some subscripts.

• P11 L20: this is a cool finding but does not readily jump out in Figure 5. I suggest adding a fourth panel showing a difference between the 5b and 5c (or 5a) spectra and zooming in the m/z scale to show the just a few –OD containing sticks (e.g., from m/z 310 to 360).

• Figure 5: There is enough empty space in each subfigure to include the dinitrite:nitrite ratio value. I suggest adding this in to quantify the “highest ratios observed in 5b” statement on P11 L24.

• Figure S7: units of OH$_{exp}$ are incorrect on both X- and Y-axes (s, not s$^{-1}$).

References:


