

Interactive comment on “HO_x and NO_x production in oxidation flow reactors via photolysis of isopropyl nitrite, isopropyl nitrite-d₇, and 1,3-propyl dinitrite at = 254, 350, and 369 nm” by Andrew Lambe et al.

Anonymous Referee #3

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Review of Lambe et al., AMTD, 2018

Summary and Recommendation

Authors introduce a new method for investigating NO_x-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 NO_x-dependent SOA formation pathways in OFRs for three primary reasons. First, because it does not require extremely high

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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 NO_x analyzer, and they had to use a photochemical model to estimate NO_x in lieu of a direct measurement. Second, the NO_x 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 NO_x 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.

Major Comments

Elaborate on alkyl nitrite interference with NO_x 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?

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

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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.

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 NO_x 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.

Figure 2: The explanation for lower OH_{exp} 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 $\sigma_{\text{iPrONO};369} \ll \sigma_{\text{iPrONO};254}$ (Table 1), the effect of photolysis wavelength on [NO₂] is proportional to σ_{iPrONO} , as expected” and how that relates to reduced OH exposure at 254 nm. The other explanation for reduced OH_{exp} 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.

Section 3.4: OH_{exp} 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?

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

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conditions, particularly for NO:NO₂ ratios and RO₂:HO_x? Are there certain conditions that should particularly be avoided? Can you make those more clear as well?

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 NO_x pathways?

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 NO_x pathway (for example, N₂O addition).

Minor Comments

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?

Interactive comment on Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2018-225, 2018.

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