

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 $\lambda = 254, 350, \text{ and } 369 \text{ nm}$ ” by Andrew Lambe et al.

Anonymous Referee #1

Received and published: 11 September 2018

The author developed a new method using alkyl nitrite photolysis as a source of OH radical and NO_x. Kinetic modeling was done to support that a much wider range of NO:HO₂ ratio (10⁻¹–10000) was achieved. They present experimental and model characterization of the OH exposure and NO_x 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 to HO_x and NO_x obtained using both isopropyl nitrite and O₃ + H₂O + N₂O methods. This new method proposed

C1

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.

Major comments: While the author uses alkyl nitrates as a source of HO_x and NO_x 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?

Specific comments: 1) P1 Line 4: Delete “t” before “ $\lambda = 254 \text{ nm}$ ” 2) P3 Line 18–22. The author tried to use a NO_x 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 NO_x 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. 3) P4 Line 20–24. To test this hypothesis, 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. 4) 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. 5) P6 Line 23–24. I suggest the author add

C2

the reference data into that plot to show directly that their results are in good agreement with literature data. 6) P8 Line 6. Add “The model results showed that” before “For [iPrONO] \leq 5 ppm”. 7) 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.

Ye, J., Abbatt, J. P. D., and Chan, A. W. H.: Novel pathway of SO₂ 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.

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