Interactive comment on "Controlled nitric oxide production via O(^{1}D)+N$_2$O reactions for use in oxidation flow reactor studies" *by* Andrew Lambe et al.

Anonymous Referee #2

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Lambe et al. presented a new method to maintain a high NO concentration in the PAM reactor in a controlled manner. They performed experiments demonstrating that N-containing highly oxidized organic compounds could be formed in the PAM by adding a few percent of N2O. Kinetic modeling was done to support that a high NO:HO2 could be achieved. If proven effective, the new method proposed by Lambe et al. would open the prospect of OFR experiments at high NO, which have previously been thought to be very difficult to conduct. However, several major issues should be addressed to convince this reviewer and the research community of the effectiveness of this method.

1. While the main goal of this paper is an experimental demonstration of proof of concept of oxidation flow reactors with a dominant contribution of the RO2+NO pathway, it

failed to provide convincing evidence that the observed N-containing product formation is due to that pathway. The authors have not ruled out peroxynitrate formation (see comment #2) or products from NO3 oxidation. Although the authors tried explaining the trend of N-containing product signals vs. NO:HO2 in Section 3.4 and Figures 4 and 5, their discussion seemed to start with the assumption that most N-containing products are formed by RO2+NO, i.e. organic nitrates. This assumption needs to be demonstrated. To clearly demonstrate organic nitrate formation through RO2+NO, I suggest conducting additional experiments where short-chain alkanes (e.g. butane) are used as precursor and OH exposure is limited. In these experiments, acyl RO2 formation is limited, NO3 addition is impossible, RO2 autoxidation is unlikely, and CIMS data should be much simpler to analyze and could contain much clearer information pointing to organic nitrate formation.

2. This study completely ignored the possibility of peroxynitrate formation in the PAM. Acylperoxynitrates are relatively stable, especially at short residence times such as in the PAM. NO3- CIMS is unable to distinguish organic nitrates from acylperoxynitrates. Showing tentative structure attribution in e.g. Figure 4 without emphasizing the caveats is very misleading. If N-containing products are mostly acylperoxynitrates formed by RO2+NO2, the new method in this paper may not be as useful as claimed. It should be demonstrated that acylperoxynitrates are not dominant products in the experiments shown in this paper.

3. This paper claimed that high NO concentrations and a variable NO:HO2 were obtained by the new method. But these quantities were all only calculated by a model. If these quantities are measured, the claims would be much more convincing, especially for a study that is mainly an experimental demonstration of proof of concept. NO is easy to measure and a method for measuring HO2 with CIMS has recently been published (Sanchez et al., 2016).

4. At the highest UV used in this study (3.2x10^15 ph cm-2 sec at 254 nm), the UV light can be estimated to destroy >90% O3 by the end of a residence time of 80 s.

Moreover, NO, HO2, OH etc. can also consume O3. As a result, both OH and NO production, sustained by O3, would be greatly reduced then and the chemistry close to the exit of the reactor would remarkably deviate from the authors' original design. However, most experiments in this study were conducted at (nearly) the highest UV. The authors should clarify the impact of O3 being largely destroyed on the chemistry in the PAM.

In addition, the following issues should also be addressed to improve the manuscript.

In the modeling of this study, it is unclear whether the effect of VOCs in affecting the OH concentration (by shortening OH lifetime) has been considered. If it has already been considered, this should be clarified.

Organic ozonolysis and NO3 reactions may be important compared to VOC reactions with OH in the PAM. In particular, a-pinene can be consumed by as much as 40% by NO3 as mentioned in the paper. The authors should rule out interferences due to NO3 reactions in the observed MS spectra and discuss the importance of organic ozonolysis relative to reactions with OH.

Page 5, Line 16: this reaction leads to total N in the model being unconserved. It is unclear to me if this reaction plays a major role. If not, it should be stated for clarity; otherwise, total N-containing species could be significantly underestimated by the model and a correction to this problem would be needed.

Page 6, Line 15: it is stated that at lower [N2O], increasing [O3] increases [NO]. But this is not clear, since both NO production and loss are approximately proportional to [O3] and change in [O3] would have little effect. If the authors did observe this, they need to provide more detail and explain its cause better.

Figures 2 and 3: according to Hyttinen et al. (2015), high HNO3 concentrations can significantly bias the sensitivities of NO3- CIMS to different highly oxidized compounds. If calibrations for CIMS data were not accordingly performed, CIMS signals may not be

considered proportional to concentrations and it is better to not show signal pie charts, which implies the proportionality, and to highlight this caveat in the text.

Other minor corrections:

Page 1, Line 17: it would be better to use the term "highly oxidized molecules (HOM)" instead of "ELVOC", as highly oxidized species may not have extremely low volatility (Kurtén et al., 2016).

Page 3, Line 16: "condensible" should be "condensable"

Page 5, Line 4: "+M" should be added on both sides of the chemical equation.

Page 9, Line 4: a space needed between "into" and "C5H7O6-11NO3"

References: Hyttinen, N., Kupiainen-Määttä, O., Rissanen, M. P., Muuronen, M., Ehn, M. and Kurtén, T.: Modeling the Charging of Highly Oxidized Cyclohexene Ozonolysis Products Using Nitrate-Based Chemical Ionization, J. Phys. Chem. A, 119(24), 6339–6345, doi:10.1021/acs.jpca.5b01818, 2015.

Kurtén, T., Tiusanen, K., Roldin, P., Rissanen, M. P., Luy, J.-N., Boy, M., Ehn, M. and Donahue, N. M.: α-pinene Autoxidation Products May Not Have Extremely Low Saturation Vapor Pressures Despite High O:C Ratios, J. Phys. Chem. A, doi:10.1021/acs.jpca.6b02196, 2016.

Sanchez, J., Tanner, D. J., Chen, D., Huey, L. G., and Ng, N. L.: A new technique for the direct detection of HO2 radicals using bromide chemical ionization mass spectrometry (Br-CIMS): initial characterization, Atmos. Meas. Tech., 9, 3851-3861, doi:10.5194/amt-9-3851-2016, 2016.