Interactive comment on “Organic peroxy radical chemistry in oxidation flow reactors and environmental chambers and their atmospheric relevance” by Zhe Peng et al.

Anonymous Referee #2

Received and published: 29 October 2018

This manuscript describes the use of a chemical model to evaluate the use of oxidative flow reactors. Overall, the work is important for groups using oxidative flow reactors, and includes a high quality analysis of the chemistry in those flow reactors, and should be published subject to appropriate revision. However, I have a few qualms that should be addressed by the authors, noted below.

It is only a handful of groups that use OFRs, and the authors should address the generalizability of their research. Aside from acting as a handbook for OFR users, are there general notes on tropospheric chemistry that the authors can provide to the reader? For example, the relative importance of the different fates of RO2 is generally interesting, and a clear summarizing point from that first figure could be of use and generally interest.

The authors discuss RO2 as a general radical term, and in general their analysis makes sense from that perspective. However, in high NOx environments, RO2+NO dominantly produces RO+NO2, but sometimes produces organic nitrates (RONO2). The frequency of this branching will depend on the chemical identity of the RO2 precursor. I suspect this chemistry will impact the rates and radical balance in the OFR+N2O experiments. The authors include this reaction in Table 1, but do not discuss this reaction at all. Their model should be able to use RONO2 species to track the RO2 fate in high NOx experiments and see if the values are tropospherically relevant (i.e. will the OFR model - or OFR itself - produce a branching ratio that matches previous laboratory or field experiments?).

Finally, I would like to see the ‘Guidelines for OFR Operation’ either have a short bullet point summary of key points (or those in the Conclusions section), or be made more concise. Overall, it would behoove the authors to consider whether all the text and figures/tables are necessary to make their main points, or if there are additional places that could be removed. The paper is dense, which will reduce the readership. Reducing the number of acronyms (and making a table of whatever acronyms are left) would be very helpful for readability. There are so many ‘OFR-subversions’ that I had a challenging time reviewing portions of the manuscript.

Technical comments

line 51: remove the extra ""
line 212: I genuinely don’t understand this sentence - please clarify (i.e. an accuracy of what?)
line 352: Acyl RO2 +NO2 is typically referred to as an ‘equilibrium’, not ‘quasi-irrversible reaction’. Consider what happens as temperature is increased - in the
troposphere in summer, this equilibrium is important for most PAN-type compounds, and cannot be ignored! If this is the case in most OFRs, then there is a more serious problem with the RO2/NO2 and NO/NO2 ratios...

line 361: what are typical NO/NO2 ratios in the OFR and in the troposphere? It would be helpful to summarize in a sentence.

line 371: The sentence that states that acyl RO2 dominate aged air plumes requires a reference.

line 432: 's' on the end of 'reaction(s)' should be deleted