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Interactive comment on “Non-OH chemistry in oxidation flow reactors for the study of atmospheric chemistry systematically examined by modeling” by Z. Peng et al.

Anonymous Referee #1

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This paper describes a modeling study aimed at understanding the relative role of different oxidants within “oxidation flow reactors” (OFRs), flow tubes that have recently seen a lot of attention in atmospheric chemistry as a way to rapidly expose organic species to the equivalent of hours to days of oxidation. The aim is to assess the extent to which non-tropospherically-relevant oxidation processes may occur within such reactors. The authors conclude that under the vast majority of conditions (especially in field studies), OH oxidation dominates over photolysis and initiation by other oxidants, pointing to its utility as an “OH-only” aging reactor.

The chemical modeling is quite comprehensive, and the paper makes a very com-

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elling case for the dominance of OH oxidation for the range of compounds examined. However, this range is also the main limitation of the study – the modeling largely covers lightly-oxidized species only. Hydrocarbons and mono-substituted oxygenates are explored fairly well, but the more oxidized, multifunctional species are not. Such species are significant for two reasons: (1) they are major players in chemistry related to multi-day oxidation processes and secondary organic aerosol (SOA) formation, the main targets of OFR studies, and (2) such multifunctional species are likely to photolyze much more readily than the less-oxidized compounds covered in this work. Thus this work really only shows that OH dominates over photolysis for the oxidation of hydrocarbons and first-generation oxidation projects, but not necessarily for later-generation species. As a result, many of the strongly-worded conclusions in the manuscript, involving the dominance of OH reactions, simply might not be valid after 1-2 generations of oxidation.

Specific concerns related to these multifunctional species are:

- A few di-functional species are included (some C2-C4 species), but nothing like the sort of multi-substituted molecules that models predict to be in SOA (e.g., Johnson et al., *Env. Chem* 1, 150-165, 2004; Camredon et al., *Atmos. Chem. Phys.* 7, 5599–5610, 2007) or have been recently measured using CIMS techniques. In fact even the O/C ratios of aerosol generated within the PAM (e.g., Ortega, Lambe papers) would suggest one functional group for each 1-3 carbon atoms. For these molecules, there is a good chance that several of them will be located on adjacent carbon atoms, potentially leading to conjugated systems with much higher cross sections than from any of the individual functional groups. (The C-C bonds in between these functional groups may also be weakened, increasing dissociation quantum yields.)

- Some broad generalizations are made about the photolysis of nitrates and peroxides (e.g., page 23555 line 5). However only one nitrate (with 3 carbon atoms) and one peroxide (with 1 carbon atom) were actually studied. (PAN has a peroxy group - given it has no C-O-N bonding moiety, it is not truly a nitrate – and hydroperoxyenal

cross sections have never actually been measured, but rather only estimated based on cross sections of similar but nonperoxidic species.) Larger or more functionalized species may well exhibit very different photolytic behavior.

- The choices for SOA components (Table S6) are non-obvious. I understand that due to the lack of data, surrogate compounds need to be used. But as described above, SOA molecules will mostly have more than 1-2 functional groups, and therefore may absorb light much more strongly than any of the species listed. There may well also be intermolecular interactions that affect absorption further. The values given should thus be treated as strict lower limits, not averages. In fact, recent measurements find the cross section of α -pinene+O₃ SOA to be about 3×10^{-19} cm² (Wong et al., JPCA 119, 4309–4316, 2015), ~ 1 order of magnitude higher than any of the (non-aromatic) surrogates used in this study.

The possible fates of the later-generation, multifunctional species therefore need to be examined in more detail in this work. Of course these molecules are highly diverse, and chemical/optical data on them is very sparse. One option would be to extend the quantum chemical calculations to a range of such species, but that would probably be a major project in itself. Instead I would recommend a sensitivity study. If species absorb 254nm or 185nm light at 10x or 100x the cross sections used here, to what extent would photolysis compete with OH? If OH reaction continues to dominate, then the strong conclusions throughout the paper about the importance of OH chemistry still hold; if not, the possibility of photolysis of highly functionalized species needs to be discussed explicitly. (This would suggest an important area of future research, with measurements needed both at these low wavelengths and within the standard actinic window.)

Other comments (numbers given are page/line):

Abstract: an interesting result of this paper is that the model results suggest that under some cases, OH oxidation (relative to other oxidation channels) can actually be more

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important in the OFR than in the troposphere. This is alluded to in the mention of biogenic species reacting with O₃, but should probably be said more explicitly in the abstract.

23548 line 9: This sentence mentions peroxy-radical photolysis, which has been suggested to be a non-tropospheric reaction path within OFRs. But this is not explored anywhere in the manuscript. Either it needs to be included, or its exclusion from this paper needs to be stated.

23549/20-21: This section makes reference to the study of non-plug flow conditions in the cited Peng et al. paper. However, I didn't see any such discussion in that paper. Maybe I'm just missing it? Or did the authors use the wrong reference? (Or are they referring to an version that isn't publicly available?)

Figs 1-2 (and S1-S2): The x-axes in these plots, which are not discussed at all in the manuscript, are quite unusual, and probably should be changed. "Exposure" is best defined as "concentration times time". The x axis is given in units of cm/s; assuming the OH exposure is in the standard units (molecules-s/cm³), this would mean the authors are expressing "photon exposure" in molecule/cm², which is very hard to interpret, particularly in terms of an "exposure". The most intuitive unit to use for photon exposure is photon density times time; this would make the x axis unitless, as is the case for Figs 3-5.

Figs 2-5: This is a very complicated figure. The laboratory-study parameters might be easier to understand if they were presented as horizontal lines (ranges) rather than two markers with differently-placed labels.

23564/21: "Generation" is a confusing word here, since it usually refers to the number of reactions in a chemical mechanism required to form a specific compound. The more standard term for describing the time to an e-fold of decay is "characteristic lifetime" (e.g., Smith et al., ACP 9, 3209–3222, 2009).

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23557/section 3.1.5: It should also be noted that ozonolysis can play a major role in the oxidation of dihydrofurans, which can be formed from any number of saturated species, including anthropogenic species. This is described in multiple papers by Ziemann and coworkers; as noted in those papers, OH-only chemistry is not fully representative of the atmospheric conditions in that case, since ozonolysis (or reaction with NO₃) will dominate the fate of those compounds. This could have substantial implications for SOA formation within the OFR.

23558/28 (and elsewhere): Focusing on OH-only chemistry under conditions where OH is not the relevant atmospheric oxidant (such as in the dihydrofuran example above) does not seem to be a very important area of research. It's unclear to me then why so much text is devoted to discussing how to carry out such experiments.

23560/8: This paragraph neglects what may be the most interesting/important aspect of HO₂ chemistry, the formation of HO₂-carbonyl adducts (to form hydroxyhydroperoxy radicals). Under the very high HO₂ concentrations of the OFR, these may then form hydroxyhydroperoxides, probably to a higher extent than would happen in the troposphere. This channel should be explored here.

Table S6: Presumably these are intended to be “surrogate” SOA components, not “possible” ones, since most are far too volatile to be in the condensed phase.

Interactive comment on Atmos. Chem. Phys. Discuss., 15, 23543, 2015.

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