

Response to Reviews for the ACPD paper “Organic peroxy radical chemistry in oxidation flow reactors and environmental chambers and their atmospheric relevance”

We thank the referees for their reviews. To facilitate the review process, we have copied the reviewer comments in black text. Our responses are in regular blue font. We have responded to all the referee comments and made alterations to our paper (**in bold text**). Figures, tables, and sections in the responses are numbered as in the *revised* manuscript unless otherwise specified, while page and line numbers refer to the ACPD paper.

Anonymous Referee #1

This paper follows a number of others reporting the characterisation and optimisation of operating conditions for oxidation flow reactors (OFRs) through both experimental and modeling studies. This work focuses on a model study of the fate of organic peroxy radicals within OFRs under different operating conditions and makes comparisons to the fates of such species in the atmosphere.

R1.0) While the rationale for such a study is sound, and the methods described are appropriate, the paper is quite long for the information it contains, and there are questions as to the wider interest and novelty of the work. It would help if the authors could state the main scientific outcomes and objectives of this work more clearly, and if some detail could be provided which outlines how assumptions regarding the fates of RO₂ species have potentially impacted the results of previous studies.

We believe that our paper fulfills an important need for the rapidly growing and interdisciplinary OFR research community. The paper provides a critical assessment of best practices in the use of OFRs, and dispels common notions regarding the shortcomings of OFRs, and thus is useful. We have added the following text to the introduction (after L67 of the ACPD version) to clarify this matter:

“The use of oxidation flow reactors is growing rapidly in the atmospheric chemistry community. Some researchers have raised two concerns with regard to OFRs: (1) the chemical regime of OFRs may be unrealistic compared to the atmosphere and (2) OFRs are derivative of flow reactors with a long tradition in atmospheric chemistry, especially for chemical kinetic measurements, and thus there is not much new to be discussed or analyzed in their chemistry. While it is true that OFRs follow the tradition of flow tubes used in atmospheric chemistry, they attempt to simulate a much more complex system all-at-once and typically use much longer residence times, and thus many fundamental and practical issues arise that have not been addressed before. The need to achieve longer effective photochemical ages within a short residence time can, however, lead to

the occurrence of undesirable oxidation pathways. This paper uses computer modeling to define useful ranges in which to work.”

Therefore, we strongly believe that the present paper does address the needs of people interested in practical OFR application and those interested in the study of fundamental chemical pathways). We do make a reasonable attempt to present the methods and results in a way that is both rigorous and accessible to many OFR users with limited chemical knowledge (e.g. researchers with more of an aerosol and/or engineering training), even though to knowledgeable chemists this paper might appear to be somewhat wordy and detail-oriented.

In the response to R1.8, we have modified some text in the ACPD paper to give more details on and highlight several features of RO₂ chemistry in the atmosphere and chambers.

See also the response to comment R1.12.

R1.1) Page 4, lines 117-122: Is production of RO₂ from ozonolysis reactions or reactions between O(1D) and VOCs considered for conditions when significant ozone/O(1D) are present? Although photolysis of organics is considered, is there any consideration of photolysis of oxygenated VOCs (formaldehyde or acetaldehyde for example) which may photolyse to generate RO₂ radicals?

While RO₂ production from ozonolysis and photolysis of VOCs and their reactions with O(1D) is possible in the OH OFRs that are the focus of this paper, these non-OH pathways are significant only when OH is suppressed or not sufficiently produced, i.e. under “risky” or “bad” conditions as defined in the paper. We have previously shown that all these non-OH reactions become important for similar reasons and photolysis at 254 nm is usually the most significant type of non-OH reactions (Peng et al., 2016). The physical conditions leading to significant 254 nm VOC photolysis (non-tropospheric chemistry) are of little experimental interest. Thus we do not believe that it is necessary to include RO₂ production through non-OH pathways in this study.

We have added the following text to the end of the paragraph between L117 and L125:

“RO₂ production through other pathways, e.g. VOC ozonolysis and photolysis, is not considered, since all non-OH pathways of VOC destruction only become significant at low H₂O and/or high OHR_{ext} (Peng et al., 2016). These conditions lead to significant non-tropospheric VOC photolysis and thus are of little experimental interest.”

R1.2) Page 4, lines 133-134: The authors assume average ambient HO₂ concentrations of 1.5x10⁸ molecules cm⁻³ and kHO₂+RO₂ of 1.5x10⁻¹¹ cm³ molecule⁻¹ s⁻¹. The generic rate coefficient for HO₂ + RO₂ used seems high, for HO₂ + CH₃O₂ the rate coefficient is 5.2x10⁻¹² cm³ molecule⁻¹ s⁻¹, while that for HO₂ + C₂H₅O₂ is 6.9x10⁻¹² cm³ molecule⁻¹ s⁻¹. How do

the assumptions regarding $[HO_2]$ and kHO_2+RO_2 influence the results reported in this work? Similarly, how does the assumption regarding kRO_2+NO influence the results?

In the typical OFR experiments focused on SOA formation that we are mainly studying in this paper, CH_3O_2 and $C_2H_5O_2$ are minor contributors to the total RO_2 pool. Their formation rates through methane and ethane oxidation are very small compared to the formation of larger RO_2 radicals from other VOCs. We thus do not believe that CH_3O_2 and $C_2H_5O_2$ are important intermediates of VOC oxidation that are able to significantly alter the overall OH, HO_2 , and RO_2 budget in OFRs. In the ambient and chamber cases, OH and HO_2 have been prescribed. If CH_3O_2 and $C_2H_5O_2$ are not the RO_2 of interest (which is usually the case in SOA formation studies), the different rate constants of the reactions of CH_3O_2 and $C_2H_5O_2$ with HO_2 than the typical value used for RO_2+HO_2 in this study will have no impact on the results of the ambient and chamber cases.

For other unsubstituted and oxygenated RO_2 radicals, the rate constants of their reactions with HO_2 are indeed around $1.5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ($\sim 1\text{--}2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$; see Table 5 of Orlando and Tyndall, 2012). And the rate constants of RO_2+NO are indeed very close to $9 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (see Table 1 of Orlando and Tyndall, 2012) for most RO_2 radicals, including CH_3O_2 and $C_2H_5O_2$. Only the rate constants of acyl RO_2+NO are ~ 2 the value used in the paper.

For the modified text to clarify this issue, please refer to the response to comment R2.2.

R1.3) Page 4, line 152 (and elsewhere): Please consider changing ‘RO2s’ to ‘RO2 radicals’ or similar.

We have changed “RO2s” to “RO2 radicals” throughout the paper.

R1.4) Page 5, line 175: Please quantify the statement ‘acylperoxy nitrates barely decompose’ with an example.

We have modified the relevant sentences in L175–176 with some detail added to clarify this:

“In OFRs operated at room temperature, acylperoxy nitrates barely decompose, as their thermal decomposition lifetime is typically ~ 1 h (Orlando and Tyndall, 2012), while OFR residence time is usually a few minutes. In contrast, peroxy nitrates of non-acyl RO_2 do decompose on a timescale of 0.1 s (Orlando and Tyndall, 2012).”

R1.5) Page 6, line 205: What is the rationale for this production rate of OH? What is the VOC concentration used? (i.e. What is the pseudo-first-order rate coefficient?)

First, we would like to clarify that the text in L205 and below discusses OH loss rather than OH production. In this study, we use a proxy of external OH reactant (SO_2), but external OH reactivity (OHR_{ext} , the pseudo-first-order rate constant of OH loss due to external species (e.g. VOCs, CO, and SO_2)) is not constrained to one value. Instead, its effects are explored over a very wide range ($1\text{--}1000\text{ s}^{-1}$) across our model cases. The initial SO_2 concentration used in each model case is determined by the initial OHR_{ext} chosen for that case.

We use SO_2 as a surrogate of external OH reactants for simplicity. OHR_{ext} for VOCs evolves over time (upon oxidation of VOCs and the formation and later oxidation of the stable reaction products) (Nehr et al., 2014; Fuchs et al., 2017; Sato et al., 2017; Schwantes et al., 2017). This evolution plays an important role in OH loss over time, but is not well modeled even with explicit chemical scheme such as Master Chemical Mechanism (Sato et al., 2017; Schwantes et al., 2017). Using a slow-reacting external OH reactant, i.e. SO_2 , as a proxy can roughly account for the relatively slow decay of OHR_{ext} (compared to that of primary VOCs) due to the generation of second and later generation products. As we already stated in the ACPD paper (L208–209), this rationale has been discussed in detail in our previous papers (Peng and Jimenez, 2017; Peng et al., 2018). As this paper is already long, we prefer not to extensively discuss this approximation in the text again.

Nevertheless, for more clarity, we have modified the text in L205 to read:

“A generic slow-reacting VOC (with the same OH rate constant as SO_2) is used as the external OH reactant. Its initial concentration is determined by the initial OHR_{ext} in each model case. Then as this proxy external OH reactant slowly reacts, OHR_{ext} slowly decays. This slow change in OHR_{ext} represents not only the decay of the initial reactant but also the generation and consumption of later-generation products that continue to react with OH. The reason for this approximation has been discussed in detail in previous OFR modeling papers (Peng and Jimenez, 2017; Peng et al., 2018).”

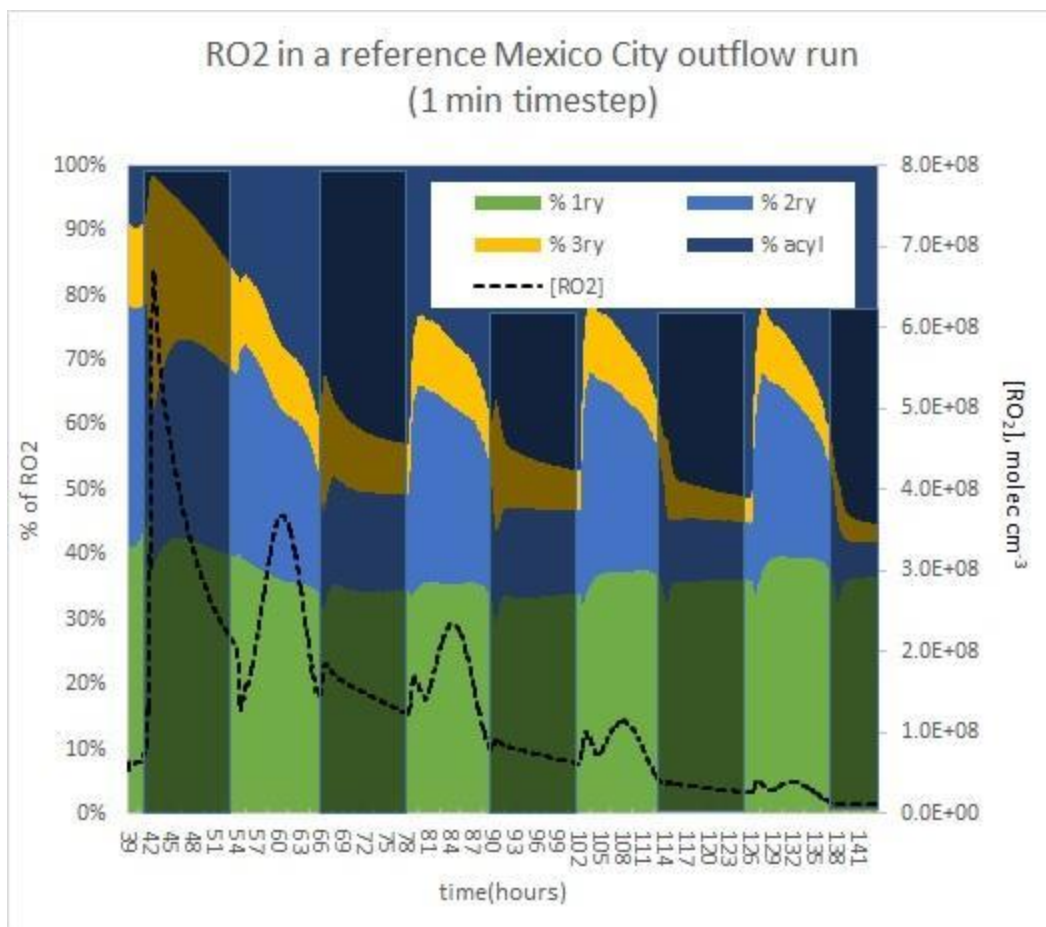
R1.6) Page 6, line 220 and page 10, line 370: Are the results from these simulations reported anywhere? How is this estimate achieved?

To address the Referee’s question, we have modified text to L219 and L369 to include more details about these calculations. The modified text in L219 reads as follows:

“We used the fully chemically explicit (automated chemical mechanism generation based on available knowledge) box-model GECKO-A (Aumont et al., 2005) to simulate OH oxidation of several simple VOCs (e.g. propane and decane) under various OFR conditions with zero-NO. We consistently find that $\beta\sim 0.3$.”

And the modified text in L369:

“However, simulations using the GECKO-A model in urban (Mexico City) and forested (Rocky Mountains) atmospheres (Figure S8) show that acyl RO₂ can still be a major (very roughly 1/3) component of RO₂ at ages of several hours or higher.



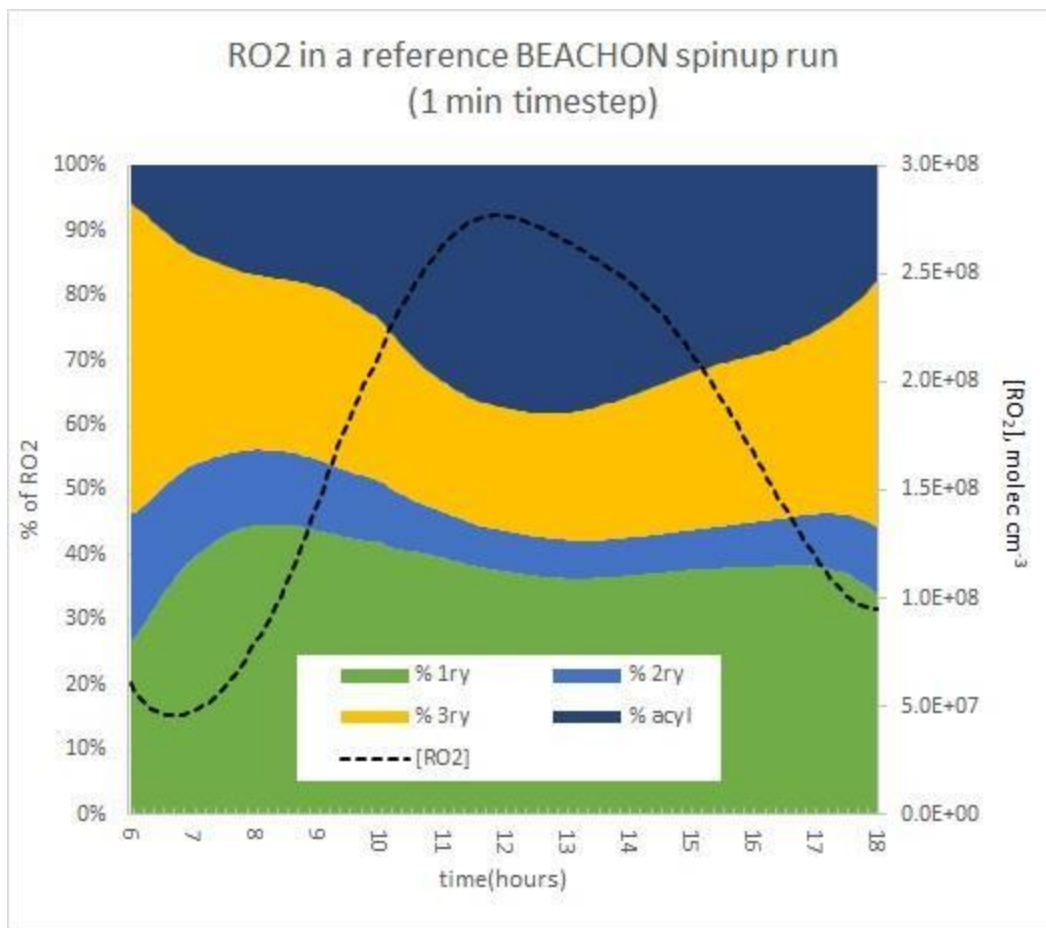


Figure S8. (a) RO₂ concentration and composition [primary (1ry), secondary (2ry), tertiary (3ry) and acyl RO₂] as a function of aging time for the simulation of a parcel of air advected from Mexico City during the MILAGRO 2006 campaign using the fully explicit GECKO-A model (Lee-Taylor et al., 2015). (b) The same for a GECKO-A simulation of air in a Rocky Mountain pine forest for the average diurnal cycle during the BEACHON-RoMBAS 2011 campaign (Palm et al., 2016; Hunter et al., 2017). Nighttime is denoted by shaded area.”

R1.7) Page 8, line 304: I'm not sure forested areas should be described as 'low VOC' given high biogenic emissions in such regions.

For more clarity, we have modified the text to L303 to read:

“Although OFRs can reasonably reproduce RO₂ fates in typical low- and moderate-OHR_{ext} ambient environments (e.g. typical pristine and forested areas; Figs. 1b,d and 3) and low-OHR_{ext} chambers, OFR185 cannot achieve relative importance of RO₂+RO₂ significantly larger than 50%, such as found in remote environments with higher VOC (e.g. P1 in Fig.

1) and high-OHR_{ext} chamber experiments (e.g. C2 and C5 in Fig. 1; the distribution for C2 is also shown in Fig. 3).”

R1.8) Page 9, line 307: Are the labels C1, C2 etc. shown in the Figures described anywhere?

We have described the typical cases corresponding to these labels in Section 3.1.1 of the ACPD paper. Nevertheless, for added clarity we have modified the paragraph starting from L262 to include more discussion about the typical ambient and chamber cases:

“In this case non-acyl RO₂ can have only three fates, i.e. RO₂+HO₂, RO₂+NO and RO₂+RO₂. The relative importance of these three fates can be shown in a triangle plot (Figure 1). The figure includes data points of OFR185 (including OFR185-iN₂O) and OFR254-70 (including OFR254-70-iN₂O), as well as several typical ambient and chamber studies, including two pristine remote area cases (P₁ and P₂) from the ATom-1 study (Wofsy et al., 2018), two forested area cases (F₁ and F₂) from the BEACHON-RoMBAS and GoAmazon campaigns, respectively (Ortega et al., 2014; Martin et al., 2016, 2017), an urban area case (U) from the CalNex-LA campaign (Ryerson et al., 2013) and five typical chamber experiment cases (C₁–C₅) from the FIXCIT study (Nguyen et al., 2014). These typical cases shown in Fig. 1 bring to light several interesting points:

- In all ambient and chamber cases, medium and slower RO₂+RO₂ contribute negligibly to the RO₂ fate. This confirms a common impression that self-/cross-reactions of many RO₂ radicals do not significantly affect RO₂ fates.
- However, if RO₂ self-/cross-reacts rapidly, RO₂+RO₂ can be the most important loss pathway among RO₂+RO₂, RO₂+HO₂ and RO₂+NO even in pristine regions with higher VOC (e.g. P₁ in Fig. 1) compared to an average pristine region case (P₂). Note that the P₁ case is still very clean compared to typical forested and urban areas (Table 2).
- Forested areas located in the same region as pollution sources are not as “low-NO” as one may expect (points F₁ and F₂ in Fig. 1). RO₂+NO contributes ~20–50% to RO₂ loss, as NO and HO₂ concentrations are on the same order of magnitude in these cases.
- RO₂+NO dominates over RO₂+RO₂ and RO₂+HO₂ in almost all urban areas. Even in relatively clean urban areas such as Los Angeles during CalNex-LA in 2010 (point U in Fig. 1), average NO is ~1 ppb, still sufficiently high to ensure the dominance of RO₂+NO among the three pathways.
- Various chamber cases in the FIXCIT campaign (low to high OHR_{ext}; low to high NO; points C_x in Fig. 1) are able to represent specific RO₂ fates that appear in different regions in the atmosphere.

On these triangle plots, points for bad OFR conditions (in terms of non-tropospheric photolysis) are not shown because of the lack of experimental interest...”

R1.9) Page 12, line 421: Subscript in 'RO2'.

We have corrected it as suggested by the Referee.

R1.10) Page 13, line 490: Should this read 'Neither is the fast RO₂ + RO₂ ...'?

We quote relevant sentences in that paragraph below:

“Since RO₂+HO₂ and RO₂+NO both can vary from negligible to dominant RO₂ fate in OFRs, chambers and the atmosphere (Figs. 1 and 2), these two pathways are not a concern in OFR atmospheric relevance considerations. Neither is the RO₂+RO₂ a major concern. Medium or slower RO₂+RO₂ is minor or negligible in the atmosphere and chambers, as well as in OFRs, as long as high OHR_{ext} is avoided in OFR254 (Fig. S2). Fast RO₂+RO₂ is somewhat less important in OFRs than in the atmosphere (Figs. 1b,d and 3), but is still qualitatively atmospherically relevant, given the uncertainties associated with the HO_x recycling ratios of various reactive systems and the huge variety of RO₂ types (and hence RO₂+RO₂ rate constants).”

We do not believe that the relevant text needs to be modified as suggested by the Referee, as the sentence “Neither is the RO₂+RO₂ a major concern” is followed by discussions on both medium/slower RO₂+RO₂ and fast RO₂+RO₂. Both types of RO₂+RO₂ are generally atmospherically relevant in OFRs.

R1.11) Page 16, line 585: Please provide a reference to the statement ‘. . . other major gas-phase radical reactions have weak or no temperature-dependence’ or compare to a typical change in rate coefficient over a similar temperature range for RO₂ + NO, RO₂ + HO₂ and RO₂ + RO₂.

We have added several examples and corresponding references into this sentence. The modified text now reads:

“A 15 K temperature increase in OFRs would lead to RO₂ isomerization being accelerated by a factor of ~3, while other major gas-phase radical reactions have weak or no temperature-dependence (e.g. ~7%, ~5%, ~6% and ~19% slow-downs for isoprene+OH, toluene+OH, typical RO₂+NO and RO₂+HO₂, respectively; Atkinson and Arey, 2003; Ziemann and Atkinson, 2012).”

R1.12) Page 16, lines 599-611: The utility of the RO₂ fate estimator is unclear. What does it do above and beyond a simple yield/budget calculations requiring knowledge of [HO₂], [RO₂], [NO]

and the corresponding rate coefficients? It would be surprising if groups performing OFR studies, or similar, weren't already able to do such calculations.

Actually, we developed the RO₂ Fate Estimator partly due to a request by a well-known atmospheric chemist who is an expert in chamber experiments. While many chamber experimentalists are aware of the importance of RO₂ fate in their laboratory experiments, often analyses are presented that are not completely consistent with each other, or that do not include all the relevant pathways. We also found relatively few available datasets in the literature for chamber experiment RO₂ fate analysis, and we recommend performing such an analysis or reporting relevant data for it in the paper. Having a standardized RO₂ fate estimator available may facilitate some of these tasks.

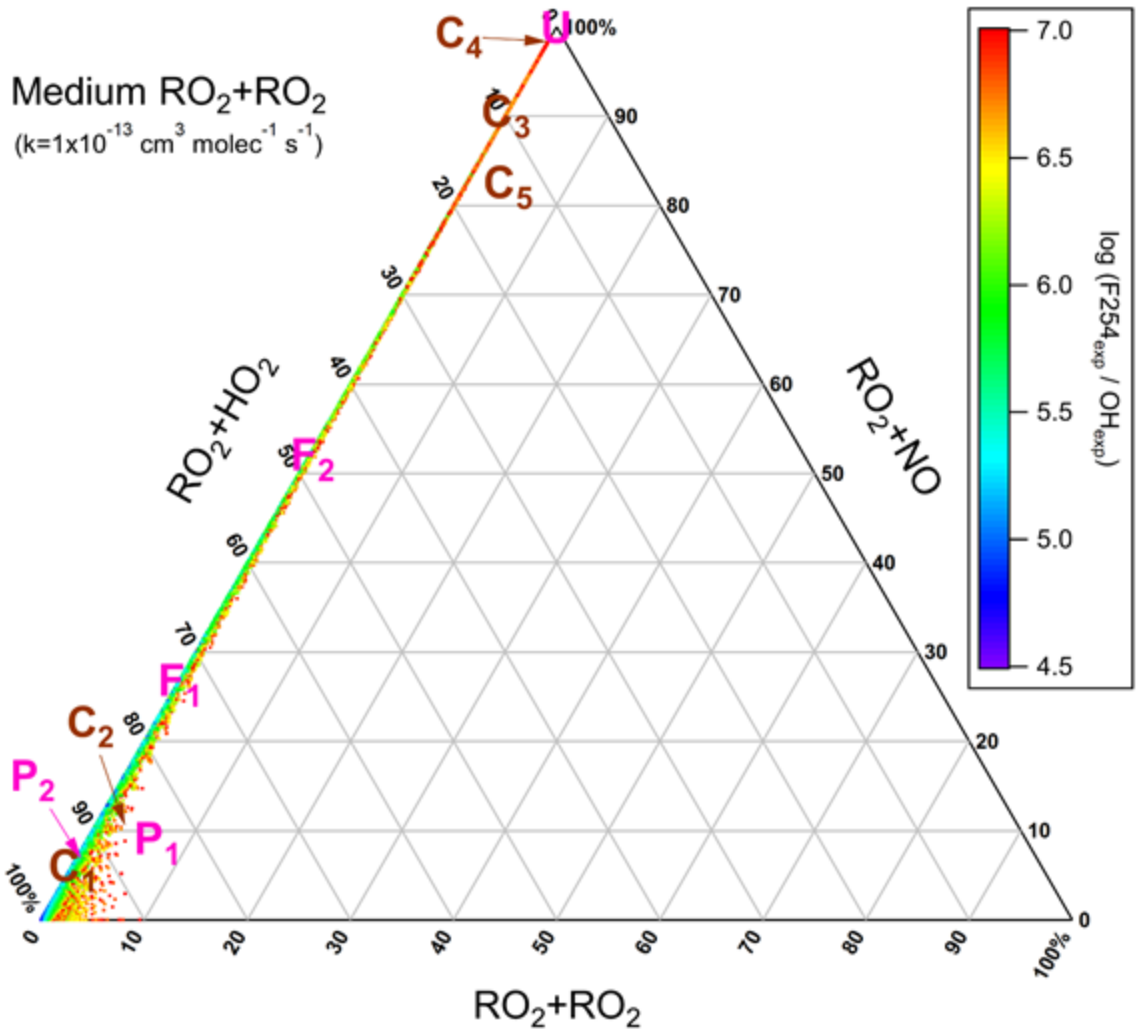
For OFR users, their awareness of the importance of RO₂ fate analysis may generally be lower than chamber experimentalists, as many of these groups have aerosol science or engineering backgrounds (e.g. aerosol optics and emission control of sources such as motor vehicles). As a result, RO₂ fate has rarely been reported in OFR studies. A user-friendly tool for these OFR practitioners to analyze this relatively complex problem would be very useful. Also quantities such as HO₂ concentration in OFRs are indeed very hard to measure, and many OFR users do not have tools to assess them independently. The estimation equations for these quantities embedded in the OFR RO₂ Fate Estimator makes realistic analyses of RO₂ fate in OFRs possible.

Therefore, we believe that both of our RO₂ Fate Estimators are of great practical interest and do not modify this paragraph (L599–611).

See also the response and added text in response to comment R1.1.

R1.13) Figure 1: The labels C1, P1, U etc. are unclear and/or overlapping with other labels on the plots.

We have modified all triangle plots to avoid overlap of the case labels. Below is an example (Figure 1a).



Anonymous Referee #2

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.

R2.1) 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.

We would like to clarify that OFRs are not only used by a handful groups. Currently there are ~50 research groups worldwide that use OFRs and this number is increasing very rapidly (probably by 10–15 groups per year). According to Google Scholar, the annual number of publications concerning OFRs has reached ~1/3 of that concerning traditional chambers and is increasing exponentially. We can comfortably claim that OFR has already become a mainstream atmospheric chemistry research tool. A study focused on such a tool, while comparing with the traditional tool (chambers) and the atmosphere, has enough scientific interest and practical importance to stand on its own.

Nevertheless, to address the Referee's concern, we have modified the text in Section 3.1.1 to provide more details of RO₂ fates in the troposphere and chambers. Please refer to the response to comment R1.8 for the modified text.

R2.2) The authors discuss RO₂ as a general radical term, and in general their analysis makes sense from that perspective. However, in high NO_x 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 NO_x 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?).

In the model, we focus on simulating generic RO₂ concentration and do not explicitly consider subsequent reactions of the products of RO₂ loss pathways. The overwhelming majority of NO_x in OFR-iN₂O exists in the form of NO₂ and NO₂ is dominantly produced from the oxidation of NO by O₃, HO₂ and OH (Peng et al., 2018), whose concentrations are orders of magnitude higher than corresponding ambient values. In the ACPD paper, we have already shown that RO₂ concentration in OFRs cannot be enhanced as much as O₃, HO₂ and OH. Therefore, whether a minor fraction of NO reacted with RO₂ produces NO₂ or not has virtually no impact on NO₂ concentration in OFR-iN₂O. Also, the HO₂ production from the reaction of RO with O₂ is already implicitly accounted for by the HO_x recycling described by β (see Section 2.3). In theory the RONO₂ formation branching ratio may affect β, but this impact should be small compared to the total HO_x recycling and generally negligible compared to the total HO_x production (Peng et al., 2015). As a result, subsequent reactions of the products of RO₂+NO and their branching ratios do not significantly affect the HO_x and NO_x balances in the simulations of OFR-iN₂O.

For simplicity, we do not specify the branching ratios of the RO+NO₂ and RONO₂ channels. As long as the relative contribution of RO₂+NO to the fate of RO₂ of interest in OFRs is close to that in other chamber or field experiments, the fractions (yields) of RO and RONO₂ in the total amount of the products of RO₂ loss pathways will also be close to those in other chamber or field experiments. Practically, readers can easily obtain those yields by multiplying the relative contribution of RO₂+NO by the branching ratios for RO₂ of interest.

For added clarity, we have modified the text to L145 to read:

“Recommended general rate constants are available for RO₂+HO₂ and RO₂+NO (Ziemann and Atkinson, 2012; Table 1), albeit with some small dependencies on the type of RO₂ and a few deviations that are slightly larger but not important for the overall chemistry (e.g. CH₃O₂ and C₂H₅O₂ for RO₂+HO₂). We use these recommended values for generic RO₂ in this study. RO₂+NO has two main product channels, i.e. RO+NO₂ and RONO₂, whose branching ratios are RO₂-structure-dependent (Ziemann and Atkinson, 2012). We do not include these product channels in this study, since they have negligible impacts on the chemical scheme described here. This feature results from two facts: i) we focus on the generic RO₂ and do not explicitly consider the chemistry of products of the different RO₂ loss pathways; ii) the channel producing RO and NO₂ contributes little to NO₂ production (Peng et al., 2018).”

R2.3) 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.

We think that in Section 3.3 there is an obvious logical flow linking the points discussed, and hence prefer to make the bullet point summary in Section 4 (Conclusions) instead of Section 3.3. The modified second paragraph (starting from L630) now reads:

“Besides the above-mentioned well-known pathways, RO₂+OH and RO₂ isomerization may also play an important role in RO₂ fate and sometimes result in atmospherically irrelevant RO₂ chemistry in OFRs. Here we summarize the main findings about all the pathways and the related guidelines for OFR operation:

- **Under typical high-NO conditions, RO₂+NO dominates RO₂ fate and RO₂ lifetime is too short to allow most RO₂ isomerizations, regardless of whether in the atmosphere, chambers or OFRs, thus raising no concern about the atmospheric relevance of the OFR RO₂ chemistry.**

- Under low-NO conditions, OFR254 cannot yield any physical conditions leading to sufficiently long RO₂ lifetime for its isomerization because of the high radical levels and their resilience to external perturbations in OFR254.
- In OFR185 with strong OH production (and hence high OH), RO₂+OH and RO₂ isomerization may strongly deviate from that in the atmosphere [becoming important and negligible, respectively, for relatively rapidly isomerizing RO₂ (rate constants on the order of 0.1 s⁻¹)].
- To attain both atmospherically relevant VOC and RO₂ chemistries, OFR185 requires high H₂O, low UV and low OHR_{ext}. These conditions ensure minor or negligible RO₂+OH and a relative importance of RO₂ isomerization in RO₂ fate in OFRs within a factor of ~2 of that in the atmosphere.
- Under conditions allowing both VOC and RO₂ chemistries to be atmospherically relevant, the maximal photochemical age that can be reached is limited to a few eq. days. This age roughly covers the period required for maximum SOA formation in ambient air.
- To most realistically study much higher ages for SOA functionalization/fragmentation by heterogeneous oxidation, a sequence of low-UV SOA formation followed by a high UV condition (in the same reactor or in cascade reactors) may be needed.
- High H₂O, low UV and low OHR_{ext} in the OFR185-iNO mode can achieve conditions relevant to clean urban atmosphere, i.e. high-NO but not sufficiently high to inhibit common RO₂ isomerization.”

In addition, we have added a glossary table as a part of the appendices to clarify the meanings of the different acronyms. Unfortunately, there are indeed multiple ways of running OFRs, each having very different chemical properties. Users have to choose a specific mode for a given experiment. The mode acronyms are thus necessary when discussing the different modes and their advantages and disadvantages:

“Appendix A: Glossary of the acronyms (except field campaign names) used in the paper

OFR	oxidation flow reactor
VOC	volatile organic compound
SOA	secondary organic aerosol
H₂O	water vapor mixing ratio
OHR_{ext}	external OH reactivity (due to CO, SO₂, VOCs etc.)
PAM	Potential Aerosol Mass, a specific type of OFR
OFR185	oxidation flow reactor using both 185 and 254 nm light

OFR254	oxidation flow reactor using 254 nm light only
OFR254-X	OFR254 with X ppm O ₃ initially injected
OFR-iN ₂ O	OFR with N ₂ O initially injected
OFR185-iN ₂ O	OFR185 with N ₂ O initially injected
OFR254-iN ₂ O	OFR254 with N ₂ O initially injected
OFR254-X-iN ₂ O	OFR254-X with N ₂ O initially injected
OHR _{VOC}	OH reactivity due to VOCs
F185, F254 etc.	UV photon flux at 185 nm, 254 nm etc.
N ₂ O	N ₂ O mixing ratio
OH _{exp} , F185 _{exp} etc.	exposure (integral over time) to OH, F185 etc.

R2.4) line 51: remove the extra "(".

We have moved the second "(" in L51 as suggested by the Referee.

R2.5) line 212: I genuinely don't understand this sentence - please clarify (i.e. an accuracy of what?)

We have modified this sentence (in L212) for more clarity. Below is the modified sentence:

"The outputs of our model (e.g. species concentrations and exposures) were estimated to be accurate to within a factor of 2–3 when compared with field OFR experiments; better agreement can generally be obtained for comparisons with laboratory OFR experiments (Li et al., 2015; Peng et al., 2015)."

R2.6) line 352: Acyl RO₂ +NO₂ is typically referred to as an 'equilibrium', not 'quasi-irreversible 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...

We do not think that a temperature increase of 10–20 K will significantly change the importance of acylperoxy nitrates in OFRs. The equilibrium constant of acyl $\text{RO}_2 + \text{NO}_2 \leftrightarrow \text{acyl RO}_2\text{NO}_2$ may change substantially. The O-N bond energy of acylperoxy nitrates is ~28 kcal/mol (Orlando and Tyndall, 2012), which we take as an approximate reaction energy of their decomposition. Then a 20 K temperature increase results in the equilibrium constant shifted toward $\text{RO}_2 + \text{NO}_2$ by $\times \sim 20$. However, this shift is still too small relative to the equilibrium constant itself. For the generic acyl RO_2 in this study in an OFR at room temperature (298 K), $\text{RO}_2 + \text{NO}_2 \leftrightarrow \text{RO}_2\text{NO}_2$ has an equilibrium constant $K_1 = \sim 2 \times 10^{-8} \text{ cm}^3 \text{ molecule}^{-1}$. In a case with NO_2 of $10^{12} \text{ molecules cm}^{-3}$ (a relatively low level in typical OFR- iN_2O experiments; Peng et al., 2018), we set $K_2 = K_1[\text{NO}_2] = [\text{RO}_2\text{NO}_2]/[\text{RO}_2] = \sim 2 \times 10^4$ as the equilibrium constant for $\text{RO}_2 \leftrightarrow \text{RO}_2\text{NO}_2$ (only when $[\text{NO}_2] \gg [\text{RO}_2]$). Even if reduced by $\times 20$ by increasing temperature by 10 K, K_2 is still as high as ~ 1000 , which means that only ~ 1 part per thousand of RO_2NO_2 will be present in the reactant form. Even if acylperoxy nitrate decomposition is $\times 20$ faster than at room temperature and the formed acyl RO_2 can irreversibly react with NO and decrease acylperoxy nitrate concentration, this effect is small: typically up to $\sim 20\%$ decrease in acylperoxy nitrate and usually negligible changes in NO and NO_2 . The minor effect is due to i) acylperoxy concentration that is still very low, ii) NO concentration that is much lower than NO_2 and iii) acylperoxy nitrate decomposition lifetime that is still on the order of minutes.

We believe that it is appropriate to describe acyl $\text{RO}_2 + \text{NO}_2$ in high- NO_x OFRs as a “quasi-irreversible” reaction *at room temperature* and add “**at room temperature**” after “the quasi-irreversible reaction $\text{RO}_2 + \text{NO}_2 \rightarrow \text{RO}_2\text{NO}_2$ ” in L352 to be more rigorous.

For OFR conditions ~ 10 – 20 K higher than room temperature, since they are different than conditions in other reaction systems and that may be unclear to other researchers, we have included a summary of the discussion above in the paper. We have added the new text at the end of the paragraph starting from L583. The added text reads as follows:

“Besides, reduction of acylperoxy nitrate formation in OFRs, which may be useful to mimic some urban environments where NO plays a larger role in acyl RO_2 fate (see Section 3.1.2), is unlikely to be achieved by increasing OFR temperature. The O-N bond energy of acylperoxy nitrates is ~ 28 kcal/mol (Orlando and Tyndall, 2012), which can be taken as an approximate reaction energy of their decomposition. Then a 20 K temperature increase results in the equilibrium constant of acyl $\text{RO}_2 + \text{NO}_2 \leftrightarrow \text{acyl RO}_2\text{NO}_2$ shifted toward $\text{RO}_2 + \text{NO}_2$ by a factor of ~ 20 . However, this shift is still too small relative to the equilibrium constant itself. It can be obtained by a simple calculation that for the generic acyl RO_2 in this study in an OFR at 318 K (20 K higher than room temperature) with NO_2 of $10^{12} \text{ molecules cm}^{-3}$ (a relatively low level in typical OFR- iN_2O experiments; Peng et al., 2018), $\sim 0.1\%$ of the total amount of acyl $\text{RO}_2 + \text{acyl RO}_2\text{NO}_2$ will be present in the form of acyl RO_2 . Even if acylperoxy nitrate decomposition is $\times 20$ faster than at room temperature and the formed acyl RO_2 can irreversibly react with NO and decrease acylperoxy nitrate concentration, this effect is small: typically up to $\sim 20\%$ decrease in acylperoxy nitrate and usually negligible changes in NO and NO_2 . The minor effect is due to i) acylperoxy concentration that is still very low, ii) NO concentration that is much

lower than NO_2 and iii) acylperoxy nitrate decomposition lifetime that is still on the order of minutes.”

R2.7) line 361: what are typical NO/NO_2 ratios in the OFR and in the troposphere? It would be helpful to summarize in a sentence.

We have modified the text to L361 to include the information requested by the Referee:

“ RO_2+NO_2 is an inevitable and dominant sink of most acyl RO_2 in high- NO_x OFRs, though the extent of this dominance differs substantially between the different OFR operation modes. In OFR254-70- iN_2O , RO_2+NO makes a minor or negligible contribution to acyl RO_2 fate because the required high O_3 very rapidly oxidizes NO to NO_2 and leads to very low NO -to- NO_2 ratios (e.g. ~ 0.003 – 0.03 ; see Fig. S7). In OFR185- iN_2O , the contribution of RO_2+NO can be somewhat significant, with typical NO -to- NO_2 of ~ 0.03 – 0.4 . (Fig S7). Urban NO -to- NO_2 ratios vary widely, for example (roughly, and excluding significant tails in the frequency distributions), 0.02 – 1 for Barcelona, 0.007 – 0.7 for Los Angeles and Pittsburgh (see Fig. S7). Given these variations among different urban areas, RO_2+NO and RO_2+NO_2 for acyl RO_2 in OFR185- iN_2O can be regarded as relevant to urban atmospheres. Exceptions to the relevance of OFR185- iN_2O occur during morning rush hours (e.g. see the high NO -to- NO_2 tail for the Pittsburgh case in Fig. S7), near major NO sources, and/or in urban atmospheres with stronger NO emission intensity (e.g. Beijing, especially in winter; Fig. S7). In these cases, NO -to- NO_2 ratios may significantly exceed 1, and RO_2+NO may be the dominant acyl RO_2 loss pathway. Such high- NO conditions appear difficult to simulate in OFRs with the current range of techniques.

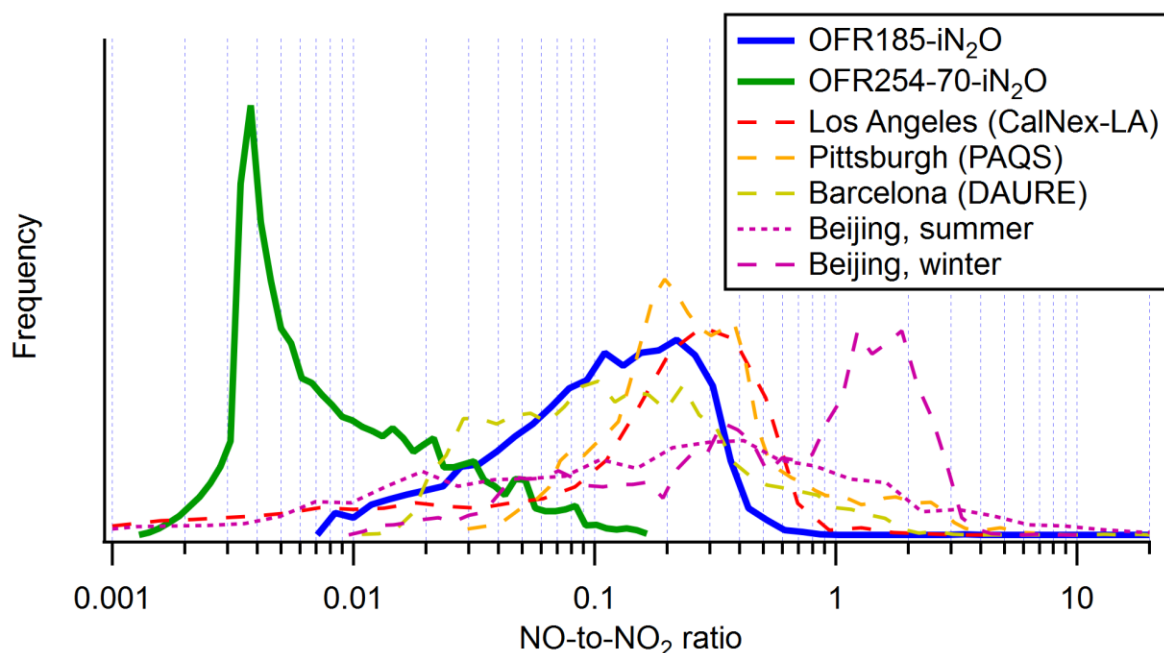


Figure S7. Frequency occurrence distributions of NO-to-NO₂ ratios for OFR185-iN₂O and OFR254-70-iN₂O model cases and measured at the Los Angeles, Pittsburgh and Barcelona ground sites during the CalNex-LA 2010, PAQS 2002 and DAURE 2009 campaigns, respectively (Zhang et al., 2005; Reche et al., 2011; Ryerson et al., 2013) and at a ground site in Beijing in both summer and winter (Hu et al., 2016). OFR cases under bad conditions are filtered out. The total areas of all distributions are identical.”

R2.8) line 371: The sentence that states that acyl RO₂ dominate aged air plumes requires a reference.

See the response to comment R1.6.

R2.9) line 432: 's' on the end of 'reaction(s)' should be deleted.

We have remove this “s” as suggested by the Referee.

Additional modification

We have discovered a bug in the OFR RO₂ Fate Estimator that affects the RO₂ fate estimation in OFR185 (low-NO mode) and fixed it in the revised Supplement.

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