

Response to editor

We thank the editor for the constructive comments that help improve the manuscript. We provide below the responses to those comments. Editor comments are in **bold**. Author responses are in plain text labeled with [R]. Line numbers in the responses correspond to those in the revised manuscript with track changes. Modifications to the manuscript are in *italics*.

In l. 84 of the revised manuscript with track changes, the authors now write:

"The HO₂ concentrations were 2-18 times (over 10 times in most of our OFR experiments) greater than the OH concentrations in the OFR. The rate coefficient for RO₂ + HO₂ was typically an order of magnitude smaller than that for RO₂ + OH (i.e., $\sim 1.5 \times 10^{-11}$ vs. $\sim 1.0 \times 10^{-10}$ cm³ molecules⁻¹ s⁻¹) (Peng and Jimenez, 2020, and references therein). We therefore expect that the RO₂ termination was dominated by RO₂ + HO₂ reactions in most of the OFR experiments herein."

My comments to this new paragraph are:

- 1. "The rate coefficient for RO₂ + HO₂ was typically an order of magnitude smaller than that for RO₂ + OH" - Use of "was" is deceptive here as it suggests that these coefficients were measured or otherwise derived in this study.**
- 2. The authors report that HO₂ concentrations are about an order of magnitude higher than OH concentrations (evidence?), but RO₂ + OH rate coefficients are about an order of magnitude higher than RO₂ + HO₂ rate coefficients, so from the reported number I would expect that both channels are of roughly similar importance. Note that Peng and Jimenez write in the mentioned reference that "Thus, RO₂ + OH may play an important role in RO₂ fate in OH OFR, when RO₂ + HO₂ is a major RO₂ loss pathway (i.e. at low NO) and the HO₂-to-OH ratio is close to or lower than 10. (Peng et al. 2019)". Hence, from my point of view, the conclusion "We therefore expect that the RO₂ termination was dominated by RO₂ + HO₂ reactions in most of the OFR experiments" is not supported by the presented evidence and reference.**
- 3. Calculation results of the PAMchem model are still not provided as requested.**

[R0] We sincerely thank the editor for the further comment and suggestion. We have revised the text and added a figure for the PAMchem model results in SI (shown below). We agree with the editor that both RO₂ + HO₂ and RO₂ + OH channels were probably of similar importance. Here is the revised text (Lines 84-89):

"The modeled HO₂-to-OH concentration ratio is about 2-18, while the rate constant for RO₂ + HO₂ is typically an order of magnitude smaller than that for RO₂ + OH (Peng et al., 2020, and references therein). Figure S1 shows the calculated contributions of various pathways to the RO₂

loss in our experiments for a given set of rate constants. Both of the $\text{RO}_2 + \text{HO}_2$ and $\text{RO}_2 + \text{OH}$ channels are important for RO_2 loss under conditions of our experiments considering the uncertainties of the estimations and the variations of reaction constants.”

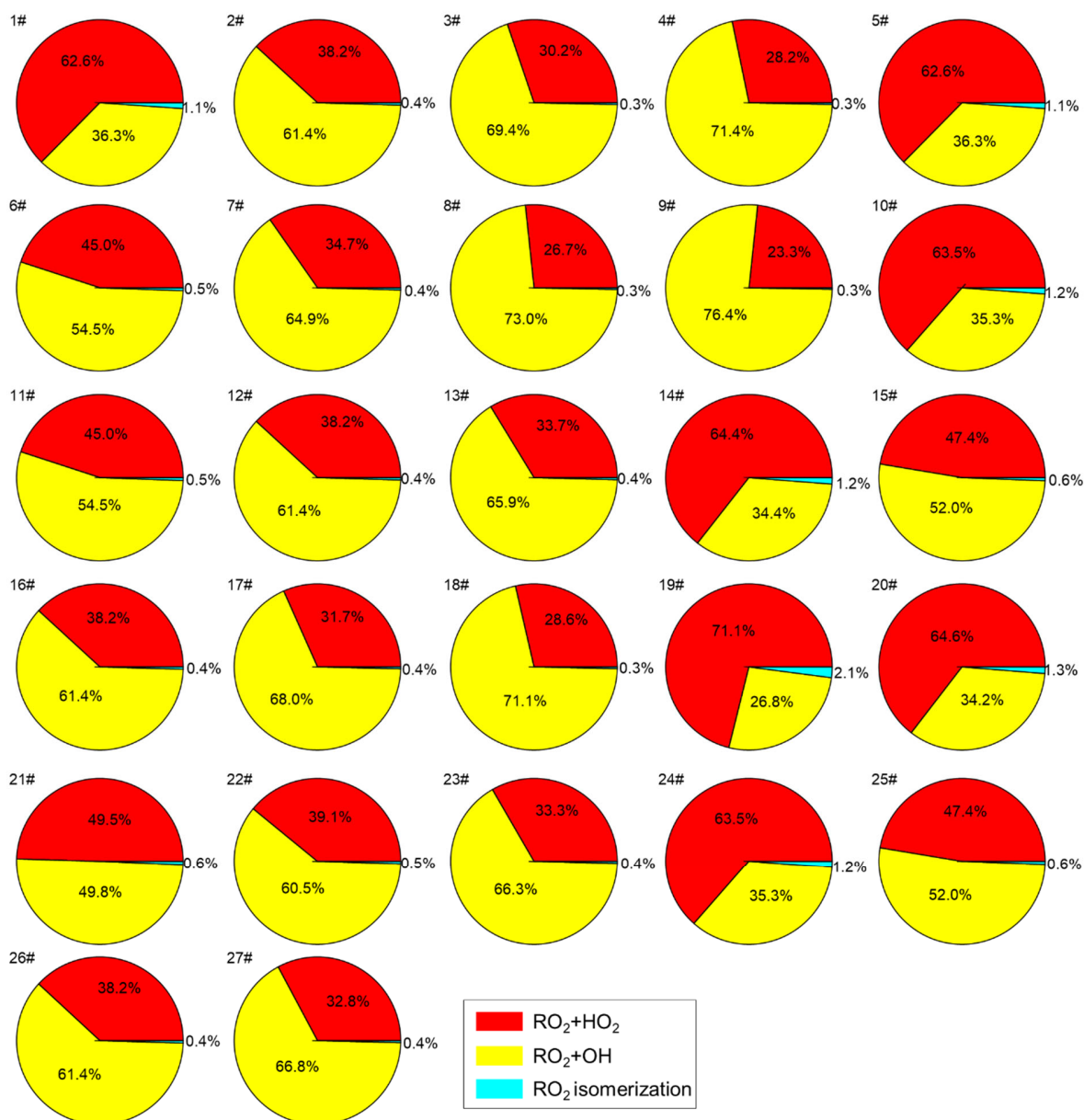


Figure S1. The relative contributions of RO_2 loss channels to the RO_2 fate calculated by using the RO_2 fate estimator (<https://sites.google.com/site/pamwiki/estimation-equations>) with the measured RO_2 concentrations, the PAMchem-model-derived OH and HO_2 concentrations, and the rate constants of $1.5 \times 10^{-11} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ for $\text{RO}_2 + \text{HO}_2$, $1.0 \times 10^{-10} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ for $\text{RO}_2 + \text{OH}$, 0.01 s^{-1} for RO_2 isomerization, and $1.0 \times 10^{-13} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ for primary $\text{RO}_2 +$

RO₂ reactions for all our experiments (Ziemann et al., 2012; Yan et al., 2016; Praske et al., 2018; Orlando et al., 2012).

Reference:

Orlando, J. J., et al., Laboratory studies of organic peroxy radical chemistry: an overview with emphasis on recent issues of atmospheric significance. *Chem. Soc. Rev.* **2012**, *41*, (19), 6294-6317.

Peng, Z., et al., Radical chemistry in oxidation flow reactors for atmospheric chemistry research. *Chem. Soc. Rev.* **2020**, *49*, (9), 2570-2616.

Praske, E., et al., Atmospheric autoxidation is increasingly important in urban and suburban North America. *Proc. Natl. Acad. Sci. U. S. A.* **2018**, *115*, (1), 64-69.

Yan, C., et al., Kinetics of the Reaction of CH₃O₂ Radicals with OH Studied over the 292-526 K Temperature Range. *J. Phys. Chem. A* **2016**, *120*, (31), 6111-6121.

Ziemann, P. J., et al., Kinetics, products, and mechanisms of secondary organic aerosol formation. *Chem. Soc. Rev.* **2012**, *41*, (19), 6582-6605.