Response to the comments of Reviewer #2

We thank Anonymous Referee #2 for the review of our manuscript. We have fully considered the comments and responded to these comments below in blue text. The revisions in the manuscript are presented in red text. Line numbers in our response correspond to those in the revised manuscript.

(Q=Question, A=answer, C=Changes in the revised manuscript)

The authors are presenting experimental results on product formation from the OH + isoprene reaction conducted in a flow-through apparatus with a residence time of about 60 s applying very high OH radical concentrations. OH radicals were produced by means of ozone photolysis in the presence of water vapor. Total peroxides were determined by an iodometric method and MVK and MACR (and other carbonyls) by means of DNPH derivatization. No direct measurements of RO2 radicals, HO2 or hydroxy hydroperoxides are provided. Based on modeling results the authors concluded that RO2 radicals mainly reacted with HO2 or via RO2 self- and cross-reactions. Nothing is said regarding the possible contribution of the RO2 + NO reaction for product formation. The authors obviously neglected the RO2 + OH reaction, even for the very high OH levels in the experiments. No explanation for that is given.

A: We are sorry that the direct measurements of RO_2 and HO_2 radicals and hydroxy hydroperoxides are beyond achievable based on our current analytical techniques. NO as an impurity in the cylinder gases (<0.2 ppbv) would react rapidly with the major oxidants in the OFR including OH, O_3, and HO_2, and be converted into NO_2 in less than 1 s (Peng and Jimenez, 2020). Thus, the contribution of RO_2 + NO reaction for MACR and MVK formation is negligible. This has been added to the revised manuscript. In the revised manuscript we have evaluated the contribution of RO_2 + OH reaction to MACR and MVK formation. The OH pathway contributes < 3 % to the detected MACR and MVK. Please refer to our response to Q3 for details.

C: (Sect. 3.3 Line 254−256)

The contribution of ISOPOO + NO reaction for MACR and MVK formation is negligible because NO as a possible impurity in the cylinder gases (< 0.2 ppbv) would be converted into NO_2 by the major oxidants (OH, HO_2, and O_3) in the OFR in less than 1 s (Peng and Jimenez, 2020).

The authors are stating as a result of their experiments increasing formation yields of MVK and MACR from the HO-C5H8O2 + HO2 reaction with rising RH, i.e., an increase of C4 carbonyl production by a factor of 5 increasing RH from "dry" to 80%. This result is very surprising and would change our understanding of product formation from OH + isoprene for low-NO conditions, as also pointed out in the manuscript based on modeling results.

I think there are some weak points in the experiment, especially in the analytical technique:

Q1: Now it´s well-known that hydroxy hydroperoxides, which should be the primary product of HO-C5H8O2 + HO2 due to our current knowledge, are labile substances that tend to decompose at surfaces finally forming the corresponding carbonyls, see f.i. doi.org/10.1002/2014GL061919. This path of heterogeneous MVK/MACR formation was neglected, or checked the authors a contribution from that? Dosing the different HO-C5H8OOH isomers should clearly show what happens during sampling and DNPH derivatization. This test is necessarily needed in order to trust the carbonyl yields. Note, the "questionable" RH dependence in MVK/MACR yields in former studies was most likely due to heterogeneous MVK/MACR production.

A1: Thank you for your suggestion. We are sorry that β-1,2-ISOPOOH and β-4,3-ISOPOOH standards are currently not available. However, we carried out a series of control experiments to estimate the amount of heterogeneous MACR and MVK production in the sampling tubes by doubling their length, and on the OFR walls by introducing another same OFR before sample collection. The changes of MACR, MVK, HCHO, and C≥3 PO concentrations in different scenarios were measured simultaneously. We also evaluated the influence of DNPH derivatization on ISOPOOH isomers based on our unpublished data. We conclude from the results that the heterogeneous formation of MACR and MVK in the sampling tubes and during DNPH derivatization is minor, while that in the OFR is major. Please refer to the following for the details.

In Exp. 1 (RH=30 %) and Exp. 2 (RH=80 %) at the outlet of the OFR when OH_{exp} is equivalent to 2.77×10^{10} molec cm^{-3} s, we doubled the length of sampling tube L1 (2.0 m, FEP, 1/8 inch o. d., labeled in Fig. 1), L2 (3.4 m, FEP, 1/4 inch o. d.), or L3 (1.0 m, FEP, 1/4 inch o. d.), or added another same OFR (OFR2) before carbonyls or peroxides sample collection, and measured how much the observed MACR, MVK, HCHO, and C≥3 PO concentrations changed. The formation and loss of MACR and MVK from ozonolysis in the sampling tubes and OFR2 are negligible (< 0.01 ppbv). We found the changes in carbonyls concentrations were less than 4 % when the sampling gases passed through the additional length of L1, L2 and L3, within the uncertainty ranges (< 5 %). The changes in C≥3 PO concentrations were less than 4% at 30 % RH and less than 7 % at 80 % RH, not obvious as well regarding the uncertainty ranges (< 10 %). However, non-negligible formation of MACR and MVK and loss of C≥3 peroxides were noticed when the sampling gases passed through OFR2 at both 30 % and 80 % RH. The carbonyls were enhanced by 8 %, and the C≥3 peroxides decreased by 14 % at 30 % RH and 31 % at 80 % RH. Consequently, corrections are needed for heterogeneous carbonyl formation in the OFR. We define the loss fraction of ISOPOOH isomers in the OFR as $LF_{OFR,4,3-ISOPOOH}$ and $LF_{OFR,1,2-ISOPOOH}$, and they can be calculated as Eq. 1 and 2:

$$LF_{OFR,4,3-ISOPOOH} = \frac{\Delta MACR_{OFR2}}{[4,3-ISOPOOH_{OFR2,IN}]} \quad (1)$$

$$LF_{OFR,1,2-ISOPOOH} = \frac{\Delta MVK_{OFR2}}{[1,2-ISOPOOH_{OFR2,IN}]} \quad (2)$$

$[4,3 - ISOPOOH_{OFR2,IN}]$ or $[1,2 - ISOPOOH_{OFR2,IN}]$ refer to the concentration of β-4,3-ISOPOOH or β-1,2-ISOPOOH at the inlet of OFR2. They are determined by multiplying the observed concentrations of C≥3 peroxides (9.2 ± 0.7 ppbv for Exp. 1 and 5.2 ± 0.4 ppbv for Exp. 2 at an OH_{exp} equivalent to 2.77×10^{10} molec cm^{-3} s) and the modeled weight of the ISOPOOH isomers (83 % for β-1,2-ISOPOOH and 16 % for β-4,3-ISOPOOH) given the loss of ISOPOOH isomers is trivial in the sampling tubes. $\Delta MACR_{OFR2}$ and ΔMVK_{OFR2} refer to the changes in MACR and MVK concentrations in OFR2. The results of LF_{OFR} at 30 % and 80 %

RH are presented in Table 2. It is noted that the LF_{OFR} in Table 2 refer to the LF of ISOPOOH isomers when the sampling gases pass through the entire OFR. The LF_{OFR} at different residence times derive from the pseudo-first-order reaction kinetic equation. Our results show that β-4,3-ISOPOOH is more labile than β-1,2-ISOPOOH, and their decomposition is positively related to RH, which is consistent with St Clair et al. (2016b). The wall loss fractions of H_2O_2 and a series of α-hydroxyalkyl-hydroperoxides (α-HHs) and peroxy acids were measured in the same OFR in our previous study (Huang et al., 2013). We found that the wall loss fraction of β-1,2-ISOPOOH is almost equivalent to that of HMHP, while that of β-4,3-ISOPOOH is twice that of HMHP.

The influence of DNPH derivatization on ISOPOOH isomers was evaluated based on our unpublished data obtained from previous isoprene + OH experiments under dry conditions. The concentration of isoprene was 600 ppbv. The photolysis of 7 ppmv H_2O_2 at 312 nm UV irradiation served as the OH source. The residence time in the OFR was 137 s. The consumed isoprene was 176 ± 8 ppbv. Carbonyls were collected with DNPH cartridges and analyzed with the same method as in our experiments. The reported MACR and MVK yields were 0.18 ± 0.01 and 0.21 ± 0.02. A box model was applied to estimate the supposed MACR and MVK yields in those experiments considering a 0.063 branching ratio for ISOPO in the HO_2 reaction of ISOPOO and a wall loss rate constant of 1.19×10^{-3} for 1,2-ISOPOOH and 3.66×10^{-3} for 4,3-ISOPOOH (derived from LF_{OFR} obtained at 30 % RH). We suggest DNPH decomposes the ISOPOOH isomers if the MACR and MVK yields in the experiments are higher than the modeled values. The modeled yield is 0.19 for MVK and 0.18 for MACR, meeting with the observed one, indicating the loss of ISOPOOH isomers during DNPH derivatization is minor.

The setup for control experiments is added as Sect. 2.3 Control experiments. The calculation of LF as well as the discussion on the influence of DNPH derivatization on ISOPOOH isomers are added as Sect. 3.1 Corrections for heterogeneous carbonyl formation in the revised manuscript.

The losses of ISOPOOH isomers on the OFR walls were considered in the data analysis. Artifacts from heterogeneous carbonyl formation account for 5−12 %

(15−22 %) and 1−9 % (5−8 %) of the observed MACR and MVK at 30 % (80 %) RH, varied with the residence time in the OFR. They were subtracted from the observed concentrations. We have corrected the yields of MACR, MVK, HCHO and C≥3 peroxides in Fig. 2 and the MACR and MVK concentrations in Fig. 5. All calculations involving MACR and MVK concentrations have been reprocessed. Please refer to the following for the major revisions in the text.

C1: (Sect. 2.3 Line 131−138)

2.3 Control experiments

β-ISOPOOH isomers are labile substances that tend to decompose at surfaces, forming the corresponding carbonyls MACR and MVK (Rivera-Rios et al., 2014), and HCHO as a by-product. Control experiments were conducted to evaluate the heterogeneous carbonyl formation in the OFR and sampling tubes. In Exp. 1 (RH=30 %) and Exp. 2 (RH=80 %) at an OH_{exp} equivalent to 2.77×10^{10} molec cm^{-3} s, we doubled the length of sampling tube L1 (2.0 m, FEP, 1/8 in. o. d., labeled in Fig. 1), L2 (3.4 m, FEP, 1/4 in. o. d.), or L3 (1.0 m, FEP, 1/4 in. o. d.), or added another same OFR (OFR2) before carbonyls or peroxides sample collection, and measured how much the observed MACR, MVK, HCHO, and C≥3 PO concentrations changed. See Sect. 3.1 for the results and discussion.

(Sect. 3.1 Line 153−191)

3.1 Corrections for heterogeneous carbonyl formation

The changes in MACR, MVK, HCHO, and C≥3 PO were measured when additional L1, L2, L3, or OFR2 presented. The formation and loss of MACR and MVK from ozonolysis in the sampling tubes and OFR2 are negligible (< 0.01 ppbv). We found the changes in carbonyls concentrations were less than 4 % when the sampling gases passed through the additional length of L1, L2 and L3, within the uncertainty ranges (< 5 %). The changes in C≥3 PO concentrations were less than 4% at 30 % RH and less than 7 % at 80 % RH, not obvious as well regarding the uncertainty ranges (< 10 %). However, non-negligible formation of MACR and MVK and loss of C≥3 peroxides were noticed when the sampling gases passed through OFR2 at both 30 % and 80 % RH. The carbonyls were enhanced by 8 %, and the C≥3 peroxides decreased by 14 %

at 30 % RH and 31 % at 80 % RH. Consequently, corrections are needed for heterogeneous carbonyl formation in the OFR. We define the loss fraction of ISOPOOH isomers in the OFR as $LF_{OFR,4,3-ISOPOOH}$ and $LF_{OFR,1,2-ISOPOOH}$, and they can be calculated as Eq. 1 and 2:

$$LF_{OFR,4,3-ISOPOOH} = \frac{\Delta MACR_{OFR2}}{[4{,}3-ISOPOOH_{OFR2,IN}]} \quad (1)$$

$$LF_{OFR,1,2-ISOPOOH} = \frac{\Delta MVK_{OFR2}}{[1{,}2-ISOPOOH_{OFR2,IN}]} \quad (2)$$

$[4{,}3-ISOPOOH_{OFR2,IN}]$ or $[1{,}2-ISOPOOH_{OFR2,IN}]$ refer to the concentration of β-4,3-ISOPOOH or β-1,2-ISOPOOH at the inlet of OFR2. They are determined by multiplying the observed concentrations of C≥3 peroxides (9.2 ± 0.7 ppbv for Exp. 1 and 5.2 ± 0.4 ppbv for Exp. 2 at an OH_{exp} equivalent to 2.77×10^{10} molec cm^{-3} s) and the modeled weight of the ISOPOOH isomers (83 % for β-1,2-ISOPOOH and 16 % for β-4,3-ISOPOOH) given the loss of ISOPOOH isomers is trivial in the sampling tubes. $\Delta MACR_{OFR2}$ and ΔMVK_{OFR2} refer to the changes in MACR and MVK concentrations in OFR2. LF_{OFR} at 30 % and 80 % RH are presented in Table 2. It is noted that the LF_{OFR} in Table 2 refers to those values when the sampling gases pass through the entire OFR. The LF_{OFR} at different residence times derive from the pseudo-first-order reaction kinetic equation. Our results show that β-4,3-ISOPOOH is more labile than β-1,2-ISOPOOH, and their decomposition is positively related to RH, which is consistent with St Clair et al. (2016b). The wall loss fractions of H_2O_2 and a series of α-hydroxyalkyl-hydroperoxides (α-HHs) and peroxy acids were measured in the same OFR in our previous study (Huang et al., 2013). We found that the wall loss fraction of β-1,2-ISOPOOH is almost equivalent to that of HMHP, while that of β-4,3-ISOPOOH is twice that of HMHP.

The influence of DNPH derivatization on ISOPOOH isomers was evaluated based on our unpublished data obtained from previous isoprene + OH experiments under dry conditions (600 ppbv isoprene + 7 ppmv H_2O_2 + 312 nm UV irradiation). Carbonyls were collected with DNPH cartridges and analysed with the same method as in our experiments. The reported MACR and MVK yields were 0.18 ± 0.01 and 0.21 ± 0.02. A box model was applied to estimate the supposed MACR and MVK yields in those experiments considering a 0.063 branching ratio for MACR or MVK formation in the HO_2 reaction of ISOPOO and a wall loss rate constant of 1.19×10^{-3} for β-1,2-ISOPOOH and 3.66×10^{-3} for β-4,3-ISOPOOH (derived from LF_{OFR} obtained at 30 % RH). We suggest DNPH decomposes the ISOPOOH isomers if the MACR and MVK yields in the experiments are higher than the modeled values. However, their modeled yields (0.19 for MVK and 0.18 for MACR) meet with the observed ones, indicating the loss of ISOPOOH isomers during DNPH derivatization is minor.

From the above discussions, we conclude that the heterogeneous formation of MACR and MVK in the sampling tubes and during DNPH derivatization is minor, while that in the OFR is major. The losses of ISOPOOH isomers on the OFR walls were considered in the data analysis. Artifacts from heterogeneous carbonyl formation account for 5−12 % (15−22 %) and 1−9 % (5−8 %) of the observed MACR and MVK at 30 % (80 %) RH, varied with the residence time in the OFR. They were subtracted from the observed concentrations.

Table 2: Loss fractions of β-4,3-ISOPOOH and β-1,2-ISOPOOH in the OFR (LF_{OFR}) at 30 % (Exp. 1) and 80 % RH (Exp. 2).

LF_{OFR} / %	RH=30 %	RH=80 %
β-1,2-ISOPOOH	7 ± 11	23 ± 12
β-4,3-ISOPOOH	20 ± 8	54 ± 14

(Sect. 3.2 Line 206−208)

The average yields of MACR and MVK were 10.4 ± 4.5 % and 20.1 ± 5.7 % at 30 % RH (Exp. 1) and 15.4 ± 3.3 % and 34.1 ± 5.8 % at 80 % RH (Exp. 2).

(Sect. 3.3 Line 270−273)

The yield of MACR from the reaction of β 4-OH, 3-OO ISOPOO radical (β-4,3-ISOPOO) with HO_2 is 2.3 ± 4.5 % at 30 % RH and 4.3 ± 3.3 % at 80% RH, while the yield of MVK from the reaction of β 1-OH, 2-OO ISOPOO (β-1,2-ISOPOO) with HO_2 is 10.1 ± 5.7 % at 30 % RH and 16.8 ± 5.8 % at 80 % RH.

(Sect. 3.3 Line 274−276)

The yield of β 1-OH, 2-OOH ISOPOOH (β-1,2-ISOPOOH) and β 4-OH, 3-OOH

ISOPOO (β-4,3-ISOPOOH) was 47.1 ± 9.7 % and 21.0 ± 9.7 % at 30 % RH, and 33.9 ± 8.1 % and 18.6 ± 8.1 % at 80 % RH.

(Sect. 3.3 Line 285−287)

The branching ratio for MACR in the HO_2 reaction of β-4,3-ISOPOO is 0.129 ± 0.080 at 30 % RH and 0.141 ± 0.097 at 80 % RH, while that for MVK in the HO_2 reaction of β-1,2-ISOPOO is 0.230 ± 0.070 at 30 % RH and 0.345 ± 0.103 at 80 % RH.

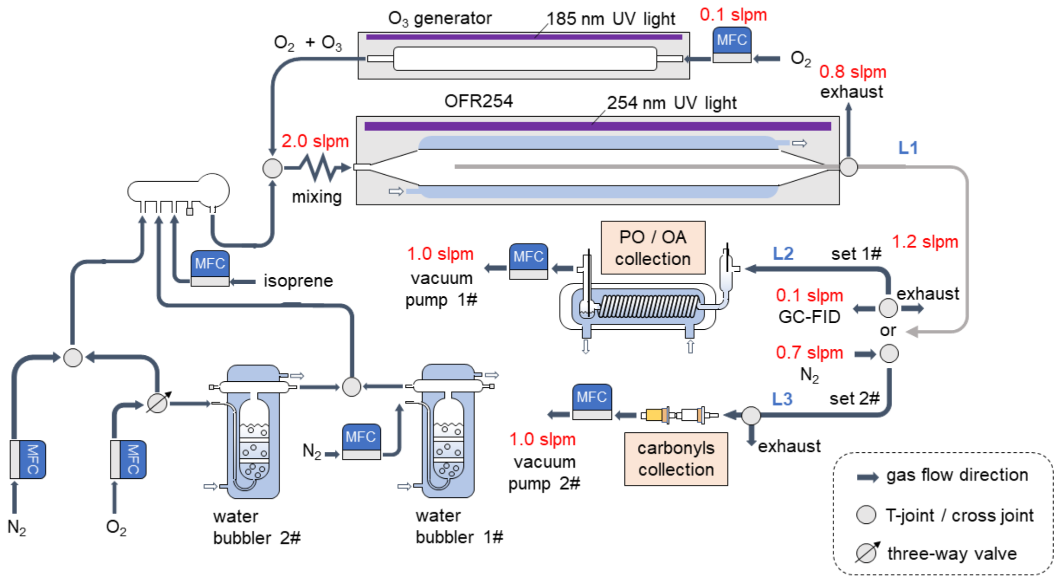

Figure 1: Overview of the experimental apparatus.

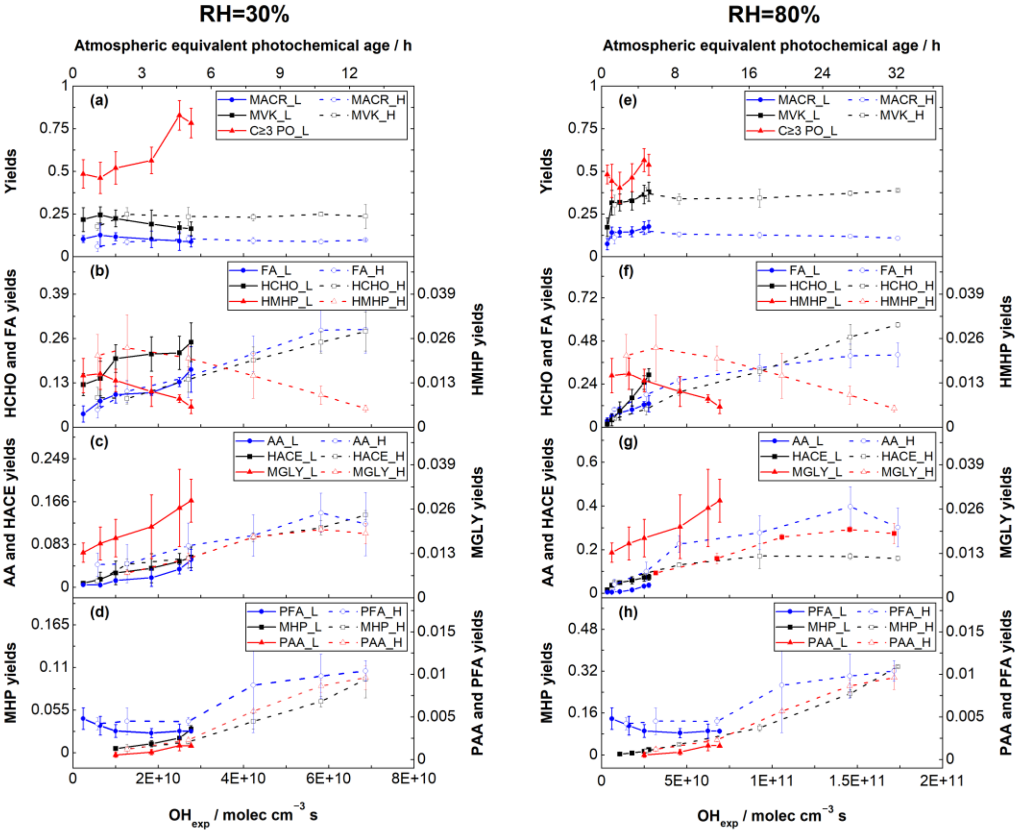

Figure 2: OH$_{exp}$-dependent overall molar yields ($Y'_{PRO,i}(t)$) of measured products at (a–d) 30 % RH and (e–h) 80 % RH in low and high OH$_{exp}$ experiments. L, yields derived from low OH$_{exp}$ experiments (Exp. 1 and 2); H, yields obtained from high OH$_{exp}$ experiments (Exp. 3 and 4). The error bars represent ± standard deviation (± SD) based on 6 measurements.

Q2: Why running the experiments with super high OH levels? There is no need for OH exposures simulating a day. A possible water-mediated HO-C5H8O2 + HO2 reaction proceeds at a time scale of seconds or less for atmospheric reactant concentrations. So it would be much better to run the reaction for almost atmospheric conditions, pushing back unwanted pathways that can become important due to the high radical levels in the experiments.

A2: The OH concentration in our experiments is on the order of 10^8 molec cm^{-3}, two orders of magnitude higher than that in the ambient atmosphere and previous studies. We ran our experiments with higher OH levels considering the following two benefits. The first is to accelerate the oxidation process and make the product concentration reach the detection limit in a short time. Assume we ran our experiments at an OH level of 4×10^6 molec cm^{-3} and 55 ppbv isoprene. According to the supposed yields and wall loss fractions of ISOPOOH isomers in our experiments, the β-1,2-ISOPOOH concentration at the outlet of the OFR would be 0.57 ppbv and 0.34 ppbv at 30 % and 80 % RH, while the β-4,3-ISOPOOH concentration would be 0.22 ppbv at 30 % RH and 0.11 ppbv at 80 % RH. The concentrations are below the detection limit (~1 ppbv) for determining total peroxides by the iodometric method. The above-mentioned concentrations are an order of magnitude lower than those in our experiments at OH 10^8 molec cm^{-3} level. An OH concentration of at least 5×10^7 molec cm^{-3} is needed to make the concentration of peroxides reach the detection limit at the outlet of the OFR. The second is to mitigate the wall loss effect. The wall loss effect of labile substances including ISOPOOH isomers would be magnified if their concentration is reduced by over 10 times in case the experiments are run at atmospheric OH levels. Maintaining a higher product concentration in the OFR is conducive to weakening the wall loss effect. We agree with you that the chemistry of ISOPOO radicals in our experiments would have some difference from that in the ambient atmosphere and unwanted pathways including the reaction of OH with ISOPOO possibly occur. The above discussions have been added to Sect. 2.1.

Moreover, we want to clarify that the discussions of water-mediated HO-C5H8O2 + HO2 reaction in this study are based on the data obtained from Exp. 1 and Exp. 2, in which the equivalent photochemical age is 0.4−5.0 hours. The data in Exp. 3 and 4 simulating higher OH exposures are used for discussions on the multi-generation photooxidation regimes of isoprene. To be more relevant to the time scales of isoprene photooxidation in the ambient atmosphere, we only selected the yields of MACR, MVK and peroxides from an OH_{exp} range of 2.4×10^9−1.8×10^{10} molec cm^{-3} s, corresponding to an atmospheric equivalent photochemical age of 0.4−3.4 h, to calculate the branching ratios for fragmentation in the HO_2 pathway (see Fig. 3) and discuss the potential water effect on this pathway. A moderate amount of isoprene (20−85 %) is consumed in this OH_{exp} range.

C2: (Sect. 2.1 Line 92−98)

The OH concentration in our experiments is on the order of 10^8 molec cm^{-3}, two orders of magnitude higher than that in the ambient atmosphere and previous studies (Paulot et al., 2009; Krechmer et al., 2015; St Clair et al., 2016a).We ran our experiments with higher OH levels considering the following two benefits. The first is to accelerate the oxidation process and make the product concentration reach the detection limit in a short time. The second is to mitigate the wall loss effect of labile substances such as ISOPOOH isomers. However, there is no denying that the radical chemistry in our experiments may have some difference from that in the ambient atmosphere and some unwanted pathways possibly occur.

(Sect. 3.3 Line 245−246)

The MACR, MVK and C≥3 peroxides yields obtained in Exp. 1 and 2 are used here to discuss the potential water effect on the reaction of β-ISOPOO via the HO_2 pathway.

(Sect. 3.3 Line 282−285)

To be more relevant to the time scales of isoprene photooxidation in the ambient atmosphere, we only selected the yields of the concerned products from an OH_{exp} range of 2.4×10^9−1.8×10^{10} molec cm^{-3} s in Exp. 1 and 2, corresponding to an atmospheric equivalent photochemical age of 0.4−3.4 h, to calculate the branching ratios. A moderate amount of isoprene (20−85 %) is consumed in this OH_{exp} range.

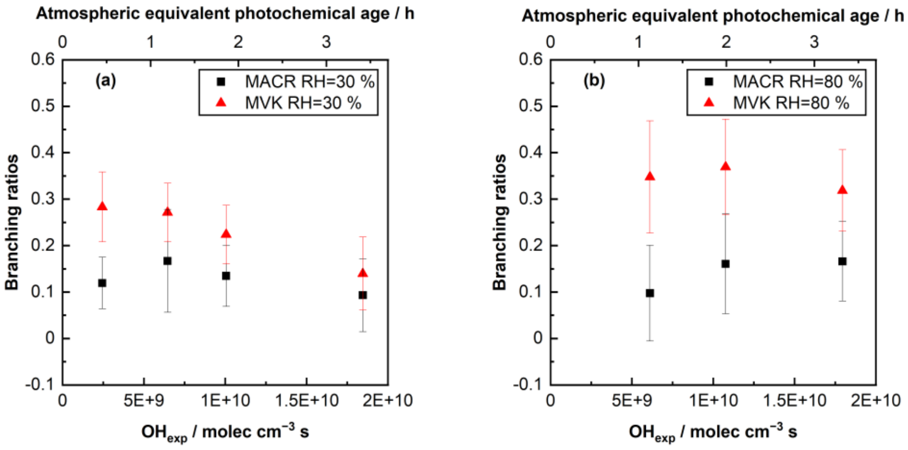

Figure 3: OH_{exp} dependent branching ratio for MACR in the reaction of β-4,3-ISOPOO with HO_2 and for MVK in the reaction of β-1,2-ISOPOO with HO_2 at (a) 30% RH and (b) 80% RH. The error bars represent ± SD of the branching ratios.

Q3: Nothing is said regarding hydrotrioxide formation in this reaction system. And also the hydrotrioxides are labile substances representing possible MVK/MACR precursors.

A3: You are right. Hydrotrioxides possibly contribute to MACR and MVK formation in our experiments. We have regarded the MACR and MVK formation from hydrotrioxide in our revised manuscript. According to Berndt et al. (2022), we suppose a branching ratio of 1.0 for isoprene hydrotrioxide (ISOPOOOH) formation in the OH reaction of ISOPOO, and a branching ratio of 0.1 for MACR and MVK formation in the OH reaction of ISOPOOOH. The rate constants are also abstracted from this study. We include the reactions of ISOPOO + OH and ISOPOOOH + OH in our model simulations. We estimate that less than 5 % of ISOPOO would react with OH in Exp. 1 and Exp. 2. The OH pathway has been included into "Fig. S2: Distribution of reaction pathways of β-ISOPOO in (a) Exp. 1 and (b) Exp. 2". We also considered the MACR and MVK formation from ISOPOOOH when modeling the evolution of their concentrations (see Fig. 5). The formation of ISOPOOOH and its subsequent decomposition contribute to less than 3 % of the detected MACR and MVK at both 30 %

and 80 % RH. The major revisions in the text are as follows:

C3: (Sect. 3.3 Line 250−252)

A recent study pointed out that the reaction of ISOPOO and OH leads to the formation of hydrotrioxides (ISOPOOOH), which are labile substances representing possible MVK and MACR precursors (Berndt et al., 2022). Thus, the OH pathway is also considered in our calculations.

(Sect. 3.3 Line 265−266)

Less than 5 % of ISOPOO would react with OH.

(Sect. 3.3 Line 314−319)

At 30 % RH, the HO_2 pathway, the RO_2 pathway, and the OH pathway contribute 18 %, 80 %, and 2 % to MACR formation, respectively. For MVK formation, the relative contributions are 60 % from the HO_2 pathway, 37 % from the RO_2 pathway, and 3 % from the OH pathway. The increase of RH to 80 % leads to a 6 % and 12 % increment of MACR and MVK derived from the RO_2 pathway. The OH pathway remains a minor contributor to MACR and MVK formation (< 2 %).

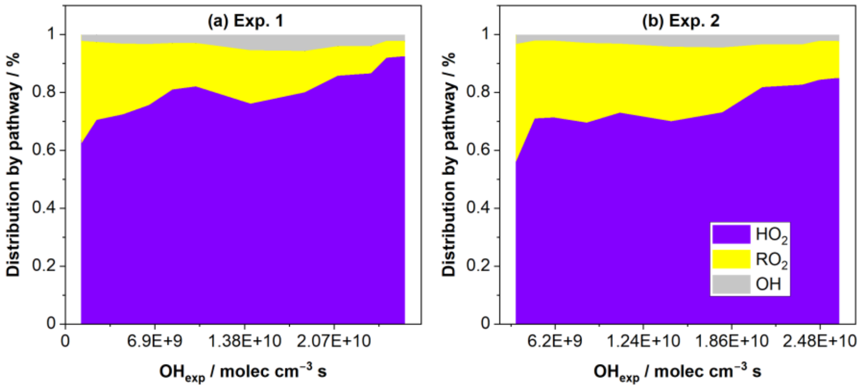

Figure S2: Distribution of reaction pathways of β-ISOPOO in (a) Exp. 1 and (b) Exp. 2.

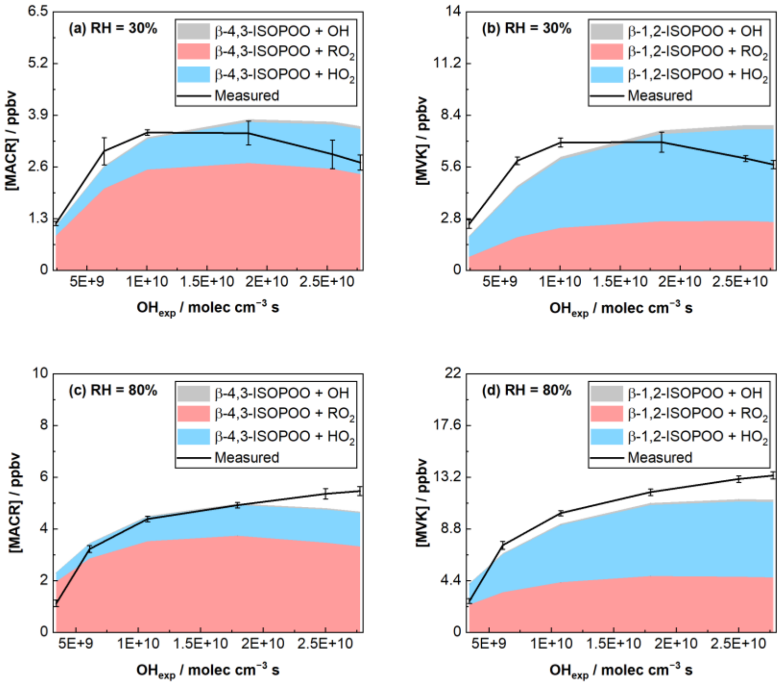

Figure 5: Comparison of the measured and modeled evolution of MACR and MVK concentrations at (a, b) 30 % RH and (c, d) 80 % RH. Updated branching ratios for MACR and MVK in the β-ISOPOO + HO$_2$ reactions were involved in the modeling. Lines and error bars (±SD), measured evolution of MACR or MVK concentrations; filled areas in red (blue, or gray), modeled MACR or MVK concentrations derived from β-4,3-ISOPOO + RO$_2$ or β-1,2-ISOPOO + RO$_2$ reactions (β-4,3-ISOPOO + HO$_2$ or β-1,2-ISOPOO + HO$_2$ reactions, or β-4,3-ISOPOO + OH or β-1,2-ISOPOO + OH reactions).

Although this work is dealing with a very interesting topic, I cannot recommend acceptance even after some modifications. I would like encourage the authors to reinvestigate the possible water-dependence in this reaction system using an improved experimental approach including the test for heterogeneous carbonyl formation.

A: We have tried our best to improve the experimental approach. We have added evaluations on the heterogeneous carbonyl formation in our revised manuscript. The heterogeneous formation of MACR and MVK in the sampling tubes and during DNPH derivatization is minor, while that in the OFR is major. Please refer to our response to Q1 for details.

References

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