

Response to the comments of Reviewer #1

We thank Anonymous Referee #1 for the review. 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)

Xu et al. investigated the effects of water on the formation of fragmentation products in isoprene photooxidation with a series of oxidation flow reactor (OFR) experiments. They found that water enhanced MVK and MACR formation and proposed water-assisted mechanisms for the reactions of β -ISOPRO with HO₂ to explain the observed fragmentation. I believe that the authors did the experiments carefully and reported a lot of useful details about them in the paper. I also think that the observations from the experiments are reliable. However, I do not agree with how the authors interpreted some key observations.

First, I find it highly implausible that HMHP formed via CH₂OH (+O₂) → HOCH₂OO (+HO₂) → HMHP in the gas phase. Theoretical calculations showed that CH₂OH and O₂ are too energetic for HOCH₂OO to be stable. Even transient existence of HOCH₂OO in this pathway will also end up with HCHO and HO₂ in picoseconds (Dibble, 2002). While I agree that the formation of HMHP as a first-generation product likely involves some C₁ fragment(s), I believe that condensed phase is needed for the ultrafast dissipation of energy excess of CH₂OH+O₂.

In the paper the authors have ruled out the reactor walls as this condensed phase. They suggested that isoprene-derived SOA may provide some aqueous phase volume. However, I do not think that isoprene-derived SOA would be enough. The SOA yield of isoprene is low even at equilibrium and without aerosol seed added a residence time of ~60 s is too short for SOA growth in OFR experiments (Palm et al., 2016).

The authors also reported much more formation of formic and acetic acids than explained by the mechanisms that the authors proposed. The strong production of FA

and AA, together with the formation of HMHP as a first-generation product, lead me to think about a possible role that aqueous-phase chemistry could play in the experiments in this study.

I suspect that the movable sampling tube might have provided the aqueous phase needed. The Teflon lining might have adsorbed water (Huang et al., 2018) and its length and surface-to-volume ratio could be high enough to affect the experimental results.

I think that the authors should verify the possibility of aqueous-phase chemistry (not just in the sampling tube as I suspected) for the formation of HMHP, FA and AA. If they were not formed in the aqueous phase, more convincing mechanisms of their formation are needed for gas-phase water-assisted mechanisms for MVK and MACR formation to be more plausible.

A: Thank you for constructive comments. You are putting forward three questions in the major comments: (1) the possibility of aqueous-phase chemistry for the formation of HMHP, FA and AA; (2) gas-phase mechanisms for HMHP formation; (3) gas-phase mechanisms for FA and AA formation. In the following we will respond to the three questions separately.

Q (1): The possibility of aqueous-phase chemistry for the formation of HMHP, FA and AA.

A (1): We did control experiments to see if HMHP, FA, and AA are formed via aqueous-phase reactions. We suppose the aqueous-phase reactions possibly take place in the coiling tube, in the sampling tubes, or on the reactor walls given that isoprene-derived SOA is not the place.

The aqueous-phase reaction of H_2O_2 and HCHO in the coiling tube is a possible source for HMHP. We estimated the amount of HMHP formed in the coiling tube based on the concentration of HCHO (calculated from its measured concentrations in the gas phase and Henry's law constant, 3242.4 M / atm) (Sander, 2015) and H_2O_2 (measured by the HPLC) in the rinsing solution and the equilibrium constant of their reaction (172 M^{-1}) (Dovrou et al., 2022). Note that the value we estimated here refers to the upper limit because the time scale of HMHP equilibration is 30–60 min (Zhao et al., 2013), yet the residence time of the rinsing solution in the coiling tube is less than 10 min

before measured by the HPLC. HMHP formed in the coiling tube consists of no more than 17 % of the detected HMHP, with an increasing proportion with OH_{exp} , and this part was subtracted from its yield shown in Fig. 2. The formation of AA and FA in the coiling tube was excluded because we analyzed the samples twice continuously (the time resolution for each measurement is 31 min) and the changes in FA and AA concentrations were within 3 %, indicating that the concentrations of FA and AA in the rinsing solution are stable within a time scale of tens of minutes.

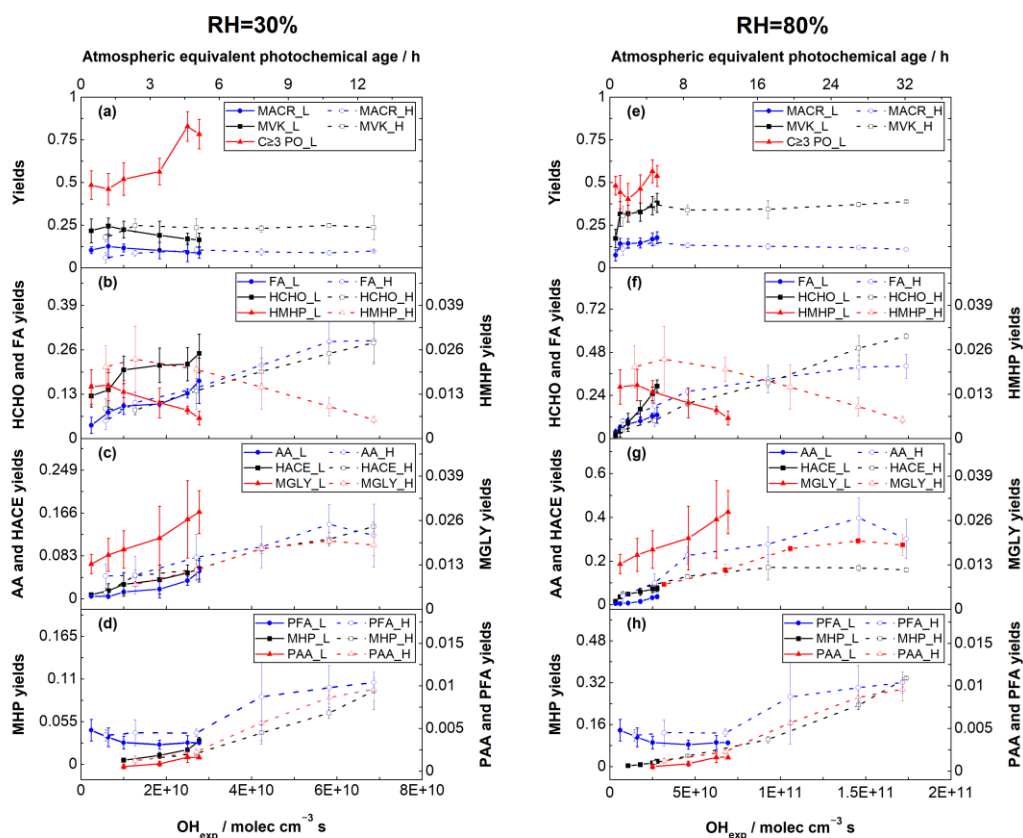


Figure 2: OH_{exp} -dependent overall molar yields ($Y'_{\text{PRO},i}(t)$) of measured products at (a–d) 30 % RH and (e–h) 80 % RH in low and high OH_{exp} experiments. L, yields derived from low OH_{exp} experiments (Exp. 1 and 2); H, yields obtained from high OH_{exp} experiments (Exp. 3 and 4). The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

To check the possibility of HMHP, FA, and AA formation in the sampling tubes, we doubled the length of sampling tube L1 (2.0 m, FEP, 1/8 in. o. d.) or L2 (3.4 m, FEP, 1/4 in. o. d.) (labeled in Fig. 1), and measured whether their concentrations changed. No obvious changes in HMHP (< 6 %), AA (< 6 %), and FA (< 4 %) were observed at

30 % and 80 % RH when the sampling gases passed through the additional length of the sampling tubes because of the extremely short residence time (0.22 s in L1 and 2.5 s in L2). The case on the OFR walls is more complicated because both photo and dark reactions may occur in the aqueous phase. We added another same OFR as we used in the experiments (OFR2) before sample collection to check the dark wall reactions. The concentrations of HMHP and FA decreased by 30 % and 5 %, respectively, due to the wall loss in OFR2, while the AA concentration increased by 10 %. We placed ~5 mL rinsing solution collected in Exp. 1 (RH=30 %) or Exp. 2 (RH=80 %) at an OH_{exp} equivalent to $2.77 \times 10^{10} \text{ molec cm}^{-3} \text{ s}$ into a quartz tube sealed at both ends and put it under the same 254 nm UV lamp as in the experiments for 60 s. We found the changes in FA and HMHP concentrations are restricted, while the AA concentration increased by 30 % after the irradiation. Consequently, we suggest the aqueous-phase chemistry on the reactor walls may have some influence on AA formation. However, its impact on FA and HMHP formation is minor.

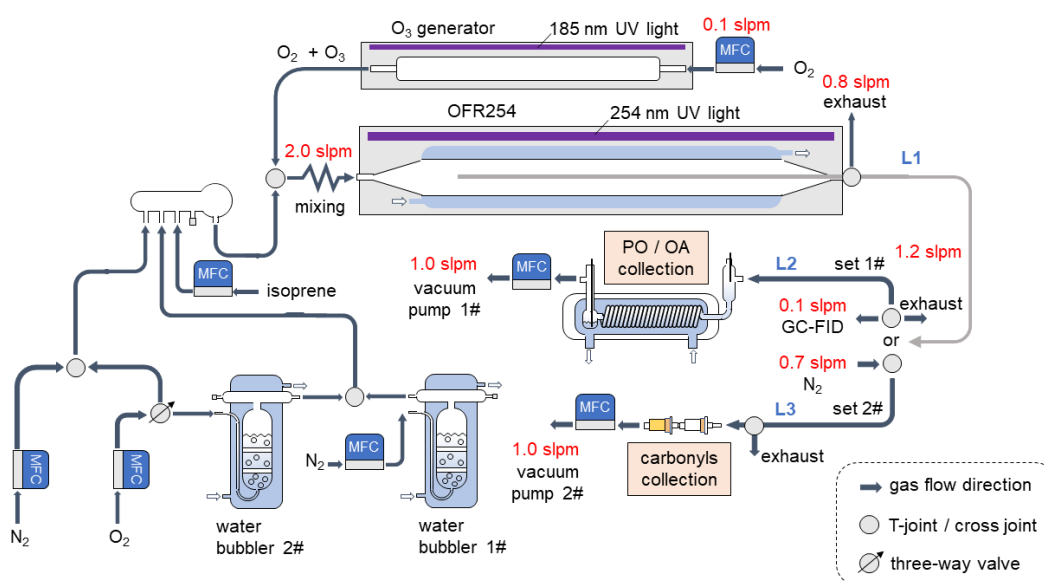


Figure 1: Overview of the experimental apparatus.

The setup of the control experiments, as described above, has been added to Sect. 2.3 Control experiments and the results and discussions are presented in the manuscript as follows:

C (1): (Sect. 2.3 Line 139–144)

Teflon tubes can absorb water, creating conditions for aqueous-phase reactions (Huang et al., 2018). To verify the possibility of aqueous-phase chemistry for the formation of HMHP, FA, and AA in the sampling tubes and the OFR, we measured the variations in HMHP, FA, and AA concentrations when doubling the length of L1 and L2, and when OFR2 is present. ~5 mL rinsing solution collected in Exp. 1 or Exp. 2 was placed into a quartz tube sealed at both ends and put under the 254 nm UV irradiation for 60 s to simulate the possible aqueous-phase photo-reaction in the OFR and check how much it would affect our results.

(Sect. 2.2 Line 116–118)

The possibility for aqueous-phase FA and AA formation in the coiling tube is excluded because continuous analysis shows that the FA and AA concentrations remain stable within a time scale of tens of minutes.

(Sect. 3.2 Line 196–199)

The reaction of H_2O_2 and HCHO in the coiling tube is a potential source for HMHP formation (Zhao et al., 2013). We estimated this part of HMHP formation based on the concentration of HCHO and H_2O_2 in the rinsing solution and the equilibrium constant of their reaction (172 M^{-1}) (Dovrou et al., 2022), and it was subtracted from the results.

(Sect. 3.2 Line 224–225)

Control experiments have excluded the possibility of HMHP formation in the sampling tubes and on the OFR walls.

(Sect. 3.4 Line 376–383)

Aqueous-phase chemistry may be a potential source for FA and AA due to the existence of water vapor. According to the control experiments, the FEP sampling tubes and OFR are not providing the aqueous phase owing to unchanged FA and AA concentrations when sampling gases passing through them. We cannot rule out the possibility for AA formation on the reactor walls under UV irradiation given a 30 % increment in AA concentration in the control experiments simulating the possible aqueous-phase photo-reaction in the OFR. Consequently, we suggest the aqueous-phase chemistry on the reactor walls may have some influence on AA formation. However, its impact on FA formation is minor.

Q (2): Gas-phase mechanisms for HMHP formation.

A (2): We agree with you that the decomposition of HOCH₂OO into HCHO and HO₂ is too fast for its reaction with HO₂ to compete (Dibble, 2002). According to the rate constants of HOCH₂OO self-decomposition and its reaction with HO₂ (Atkinson et al., 2006), only 1–3 % HOCH₂OO will react with HO₂, contributing to 6–20 % of the observed HMHP, despite of a two-orders-of-magnitude higher HO₂ concentrations in our experiments than in the ambient atmosphere. We investigated other possible sources of HMHP in the gas phase. We suggest the methyl peroxy radical (CH₃O₂) is the precursor for HMHP. OH transforms CH₃O₂ into the Criegee intermediate (CH₂OO), which reacts with H₂O to form HMHP, subsequently (Yan et al., 2016). However, given the low yield for CH₂OO (< 5 %) in this reaction and a modeled CH₃O₂ concentration on the order of 10¹⁰ molec cm⁻³ in our experiments, only 1/10 of the observed HMHP can be explained by this pathway. Other unknown pathways may exist for HMHP production. We revised the discussion for HMHP formation pathways in the manuscript as follows:

C (2): (Sect. 3.2 Line 225–233)

We suggest there are two precursors for HMHP in our experiments. One is hydroxymethyl radical (CH₂OH), which is a byproduct of the decomposition of β-hydroxy alkoxy radical (β-ISOP). CH₂OH reacts with O₂ to form hydroxymethyl peroxy radical (HOCH₂OO) rapidly. However, according to the rate constants of HOCH₂OO self-decomposition and its reaction with HO₂ (Dibble, 2002; Atkinson et al., 2006), only 1–3 % HOCH₂OO will react with HO₂, contributing to 6–20 % of the observed HMHP, despite of a two-orders-of-magnitude higher HO₂ concentrations in our experiments than in the ambient atmosphere. The other is the methyl peroxy radical (CH₃O₂). OH transforms CH₃O₂ into the Criegee intermediate (CH₂OO), which reacts with H₂O to form HMHP, subsequently (Yan et al., 2016). However, given the low yield for CH₂OO (< 5 %) in this reaction and a modeled CH₃O₂ concentration on the order of 10¹⁰ molec cm⁻³ in our experiments, only 1/10 of the observed HMHP can be explained by this pathway. Other unknown pathways may exist for HMHP production.

Q (3): Gas-phase mechanisms for FA and AA formation.

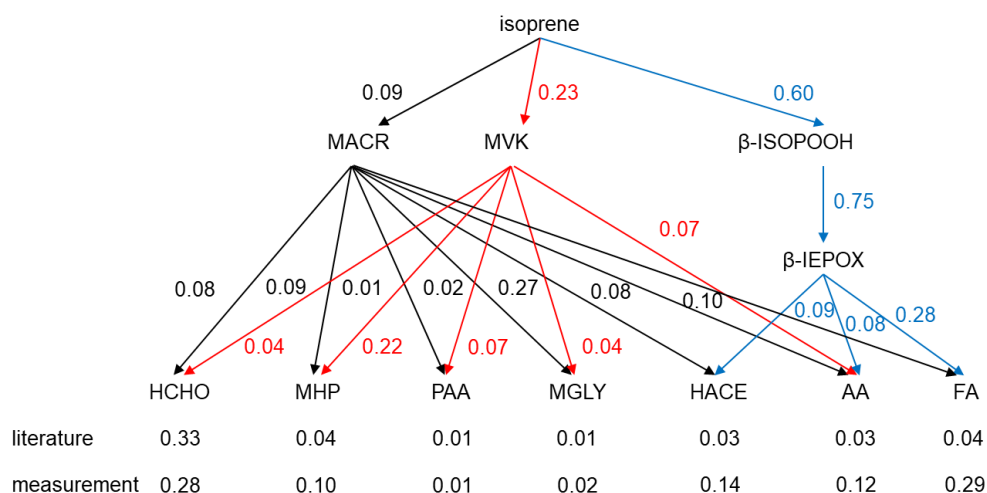
A (3): We reinvestigated the formation mechanisms for FA and AA through multi-generation reactions in the gas phase given that they are not formed via the aqueous-phase reactions in isoprene-derived SOA. We corrected the yield of FA (10 %) and AA (8 %) from MACR in Fig. 7 based on the experimental results of Link et al. (2020). There are some minor sources of FA and AA in our experiments which are not shown in Fig. 7, for example, the OH oxidation of β -4,3-ISOPROOH (2 % yield for FA) and δ -IEPOX (13 % yield for FA) (Link et al., 2020), 1,2-dihydroxy isoprene (1,2-ISOPROH, >10 % yield of FA from the H-shift and the RO₂ pathway) (Bates et al., 2021), glycolaldehyde (18 % yield for FA) (Butkovskaya et al., 2006a) and HACE (7 % for FA and 8 % for AA) (Butkovskaya et al., 2006b). However, these pathways together contribute less than 2 % to the yield of FA and less than 1 % to the yield of AA from isoprene. No literature values are available for experimental FA and AA yields from major first-generation products including MVK and β -1,2-ISOPROOH. Thus, it is inevitable to underestimate the yields of FA and AA from isoprene based on our current understanding of their formation mechanisms. It is very common for the model simulations to underestimate the observed FA and AA concentrations in laboratory research (Link et al., 2020) and ambient atmosphere (Schobesberger et al., 2016; Alwe et al., 2019). Here we tentatively put forward two additional pathways for the formation of FA and AA in our experiments. One is from the fragmentation of highly functionalized multi-generation products. Malecha and Nizkorodov (2016) reported the existence of photolabile substances in isoprene SOA which can release FA and AA during the photo-aging process. We suggest dihydroxy dihydroperoxide (ISOP(OOH)₂, C₅H₁₂O₆) and other low-volatility functionalized products containing multiple -OOH and -C=O groups formed from ISOPROOH + OH reactions account for those photoreactive products (Berndt et al., 2016; D'Ambro et al., 2017). Although the SOA yield is negligible in our experiments due to the low isoprene concentration, short residence time and a lack of seed aerosols (Palm et al., 2016), as Referee 1# pointed out, the OH_{exp} is high enough for these highly functionalized products to form and their fragmentation could be a nonnegligible source for FA and AA. Another is from the OH oxidation of hydrolyzed carbonyls in the gas phase. Both theoretical and experimental

studies have verified the feasibility of the hydrolysis of small carbonyls in water-restricted environments to form gem diols (Axson et al., 2010; Hazra et al., 2013). The OH oxidation of gem diols is a strong source of organic acids (Parandaman et al., 2018). Water vapor has converted a part of expected HCHO and CH₃CHO yields into FA and AA via the formation of gem diols. The mechanisms for multi-generation FA and AA formation in the manuscript were revised as follows:

C (3): (Sect. 3.4 Line 390–399)

Here we tentatively put forward two additional pathways for FA and AA formation in our experiments. One is from the fragmentation of highly functionalized multi-generation products. Dihydroxy dihydroperoxide (ISOP(OOH)₂, C₅H₁₂O₆) and other low-volatility functionalized products containing multiple -OOH and -C=O groups (Berndt et al., 2016; D'Ambro et al., 2017), which are precursors for FA and AA during the photo-aging process of isoprene SOA (Malecha and Nizkorodov, 2016), are possibly formed. Their further photoreaction due to a high OH_{exp} in our experiments could be a nonnegligible source for FA and AA. Another is from the OH oxidation of hydrolyzed carbonyls in the gas phase. Both theoretical and experimental studies have verified the feasibility of the hydrolysis of small carbonyls in water-restricted environments to form gem diols (Axson et al., 2010; Hazra et al., 2013). The OH oxidation of gem diols is a strong source of organic acids (Parandaman et al., 2018). Water vapor has converted a part of expected HCHO and CH₃CHO yields into FA and AA via the formation of gem diols.

(a) RH=30%



(b) RH=80%

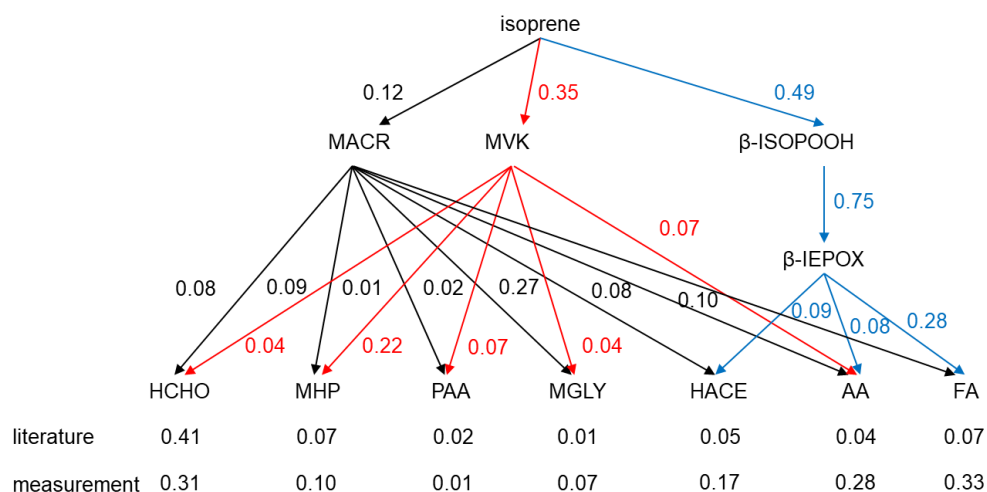


Figure 7: Comparison of the yields of multi-generation products in literature and measurement at (a) 30% RH and (b) 80% RH when atmospheric EPA equals ~15 h. Black arrows with values on the left side, MACR yield in this study and yields of MACR-derived products based on Link et al. (2020) for FA and AA and Wennberg et al. (2018) for the others; red arrows with values on the right side, MVK yield in this study and yields of MVK-derived products calculated based on Praske et al. (2015); blue arrows with values on the right side, β-ISOPROOH yield in this study, β-IEPOX yield in St Clair et al. (2016a), and yields of β-IEPOX-derived products under low NO conditions in Bates et al. (2014). The yields of HCHO and FA refer to a cocktail from the first- and multi-generation reactions.

Specific comments:

1. Line 31: further oxidation does not necessarily lead to carbon skeleton fragmentation.

A1: You are right. Further photooxidation leads to either carbon skeleton fragmentation or functionalization. We have revised this sentence on Line 31 to:

C1: (Sect. 1 Line 32–33)

Further photooxidation leads to either carbon skeleton fragmentation or functionalization, resulting in the propagation of a variety of RO₂.

2. Table 1: are the O₃ concentrations reported in this table initial or final concentrations? They are below 1 ppm. With such low O₃ concentrations and relatively high OH exposures reported here, I expect a substantial loss of O₃ in the reactor by photochemistry.

A2: We are sorry to make you confused. The O₃ concentrations reported in Table 1 are the initial concentrations at the inlet of the OFR. We measured the O₃ concentrations at the inlet and outlet of the OFR and found the photochemistry in the OFR leads to a 32 % to 48 % loss of O₃ concentrations in the range of 30 % to 90 % RH. The proportion of O₃ loss is positively correlated with RH. We have added relevant descriptions to the manuscript.

C2: (Sect. 2.1 Line 87–92)

We suggest experiments at lower initial O₃ concentrations at the inlet of the OFR (low OH_{exp} experiments, Exp. 1 and 2) represent first- to second-generation photooxidation of isoprene, while those at higher initial O₃ concentrations (high OH_{exp} experiments, Exp. 3 and 4) represent multi-generation photooxidation. The corresponding initial O₃ concentrations at 80 % RH were cut to ~40 % of those at 30 % RH to maintain OH_{exp} in a comparable range. The photochemistry in the OFR leads to a 32 % to 48 % loss of O₃ concentrations in the range of 30 % to 90 % RH. The proportion of O₃ loss is positively correlated with RH.

Table 1: Overview of the selected experimental conditions.

Exp.	[ISO] / ppbv	[O ₃] / ppbv	OH _{exp} / molec cm ⁻³ s	Atmospheric EPA / hrs	RH / %
1	55 ± 3	407 ± 3	2.4×10^9 – 3.6×10^{10}	0.4–6.6	30
2	55 ± 3	165 ± 5	3.3×10^9 – 3.8×10^{10}	0.6–7.1	80
3	55 ± 3	959 ± 16	5.8×10^9 – 7.3×10^{10}	1.1–13.6	30
4	55 ± 3	407 ± 3	7.6×10^9 – 1.8×10^{11}	1.4–32.4	80

Note: [ISO], isoprene concentrations; [O₃], initial O₃ concentrations at the inlet of the OFR. The uncertainty of OH_{exp} is within ± 15 %.

- Line 103: some hydroperoxides were reported to hydrolyze very rapidly (Qiu et al., 2019). The authors need to rule out this possible interference during sample collection or correct it.

A3: Thank you for your suggestion. Qiu et al. (2019) reported the rapid hydrolysis of α -hydroxyalkyl-hydroperoxides (α -HHs) in the aqueous phase. In our experiments, peroxides samples were collected in pH = 3.5 H₃PO₄ solution. We measured HMHP, PFA, PAA, and MHP with HPLC. Li et al. (2016) reported that the decay rate constants of HMHP, PFA, and PAA in pH = 3.5 H₃PO₄ solution are 2.5×10^{-5} , 2.9×10^{-4} , and 1.8×10^{-4} s⁻¹, respectively. The hydrolysis rate constant of MHP is $\sim 8.3 \times 10^{-6}$ s⁻¹ (Sun et al., 2021). We also measured total peroxides (TPO) with the iodometric spectrophotometric method. The total concentration of C_{≥3} peroxides can be calculated as (TPO–H₂O₂–MHP–HMHP–PAA–PFA). For Exp. 1 and 2, we suggest β -ISOPOOH dominates C_{≥3} peroxides. Fang et al. (2020) reported that β -ISOPOOH alone is stable in water and does not decompose into radicals and H₂O₂ very rapidly. The concentration of C_{≥3} peroxides in samples collected at the outlet of the OFR in Exp. 1 decayed for 20 ± 1.6 % after being placed in the dark for 2 h, indicating an overall hydrolysis rate constant of C_{≥3} peroxides as $\sim 2.8 \times 10^{-5}$ s⁻¹. We estimated that all samples are measured by HPLC or treated by KI within 20 minutes after the sampling gases contact with the rinsing solution. Consequently, we can calculate that the hydrolysis losses of HMHP, PFA, PAA, MHP, and C_{≥3} peroxides during sample collection are within 3%, 29%, 19%, 1%, and 3%, respectively. We suggest the hydrolysis of HMHP, MHP, and C_{≥3} peroxides are negligible while that of PFA and PAA may cause interference. Thus,

the yields of PAA and PFA in Figure 2 have been corrected. The details for the correction have been added in the Supplement as follows:

C3: (Sect. 3.2 Line 195–196)

Yields corrections were made to eliminate the effect of secondary OH oxidation, photolysis, hydrolysis, and wall loss of concerning products on the determination of their actual yields (see the Supplement for detail).

(Supplement Line 40–56)

Some hydroperoxides were reported to hydrolyze very rapidly. Qiu et al. (2019) reported the rapid hydrolysis of α -hydroxyalkyl-hydroperoxides (α -HHs) in the aqueous phase. In our experiments, peroxides samples were collected in pH = 3.5 H_3PO_4 solution. We measured HMHP, PFA, PAA, and MHP with HPLC. Li et al. (2016) reported that the decay rate constants of HMHP, PFA, and PAA in pH = 3.5 H_3PO_4 solution are 2.5×10^{-5} , 2.9×10^{-4} , and $1.8 \times 10^{-4} \text{ s}^{-1}$, respectively. The hydrolysis rate constant of MHP is $\sim 8.3 \times 10^{-6} \text{ s}^{-1}$ (Sun et al., 2021). We also measured total peroxides (TPO) with the iodometric spectrophotometric method. The total concentration of $\text{C} \geq 3$ peroxides can be calculated as (TPO– H_2O_2 –MHP–HMHP–PAA–PFA). For Exp. 1 and 2, we suggest β -ISOPOOH dominates $\text{C} \geq 3$ peroxides. Fang et al. (2020) reported that β -ISOPOOH alone is stable in water and does not decompose into radicals and H_2O_2 very rapidly. The concentration of $\text{C} \geq 3$ peroxides in samples collected at the outlet of the OFR in Exp. 1 decayed for $20 \pm 1.6 \%$ after being placed in the dark for 2 h, indicating an overall hydrolysis rate constant of $\text{C} \geq 3$ peroxides as $\sim 2.8 \times 10^{-5} \text{ s}^{-1}$. We estimated that all samples are measured by HPLC or treated by KI within 20 minutes after the sampling gases contact with the rinsing solution. Consequently, we can calculate that the hydrolysis losses of HMHP, PFA, PAA, MHP, and $\text{C} \geq 3$ peroxides during sample collection are within 3%, 29%, 19%, 1%, and 3%, respectively. We suggest the hydrolysis of HMHP, MHP, and $\text{C} \geq 3$ peroxides are negligible while that of PFA and PAA may cause interference. Thus, the yields of PAA and PFA have been corrected to eliminate hydrolysis losses.

4. Lines 203-204: to my knowledge, the interpretation of the MVK and MACR observed by Liu et al. (2013) has been subject to debate, with some believing that the observed MVK and MACR were artifacts during sampling.

A4: We appreciate your expertise. Referee 2# pointed out that we neglected the possible heterogeneous MACR and MVK formation in the OFR and sampling tubes, or during derivatization given ISOPOOH isomers are labile substances that tend to decompose at surfaces finally forming the corresponding carbonyls. We noticed that Liu et al. (2013) did not take this pathway of MACR and MVK formation into consideration as well. Thus, we suggest that the yields of MACR and MVK reported by Liu et al. (2013) are the upper limits via the HO₂ pathway under dry conditions. We removed the linear correlation at Line 204 in the original manuscript.

5. Figure 4: the authors need to highlight the formation of tetroxide complexes in the scheme, which is an important point in the relevant discussions in the text.

A5: We agree with you. We have highlighted the formation of tetroxide complexes in the scheme in Figure 4 in red.

C5:

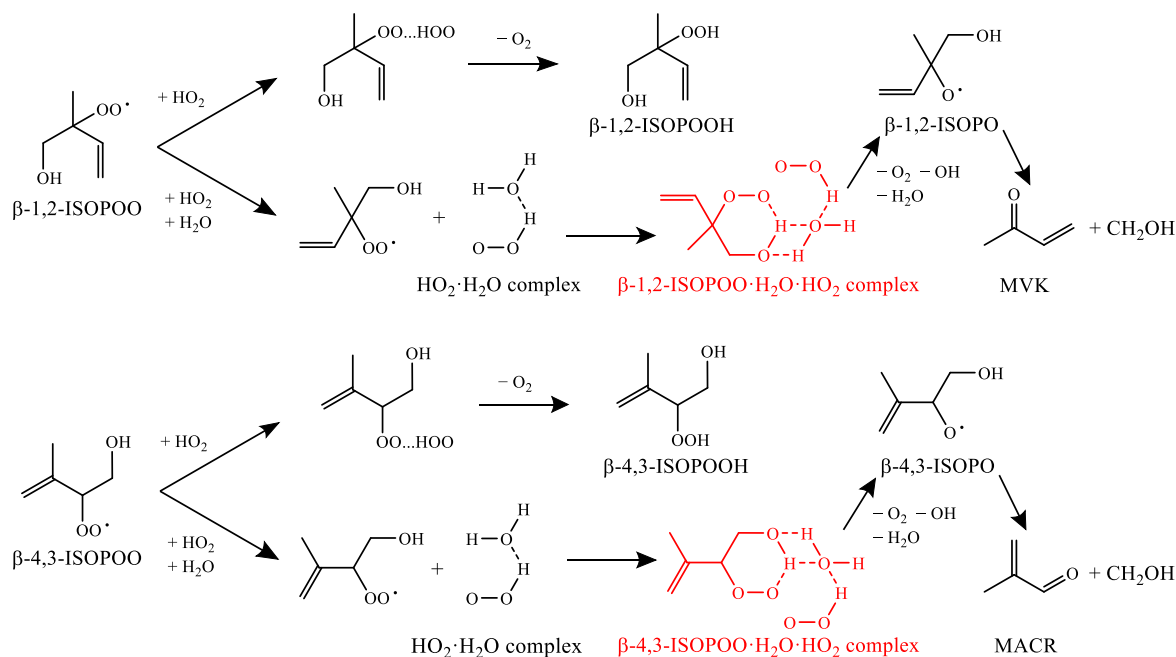


Figure 4: Suggested mechanisms for β -ISOPOO + HO₂ reactions with and without water vapor.

6. Line 280: what are the uncertainties on the relative weights of these pathways taken from MCM? Some sensitivity simulations would be preferable.

A6: Thank you for your suggestion. The relative weights of the reaction pathways of MVK-, MACR- and IEPOX-derived RO₂ are calculated following the method in Liu et al. (2013) based on the reaction rate constants of different pathways, the calculated [HO₂] and the modeled [RO₂]. According to MCM v3.3.1, MVK-derived RO₂ are HMVKA02 and HMVKBO2, MACR-derived RO₂ are MACO3, MACRO2, and MACROHO2, and IEPOX-derived RO₂ are C57O2, C58AO2, and C59O2. The reaction rate constants for HO₂, RO₂, and H-shift pathways are the weighted mean values for MACR-, MVK-, or IEPOX-derived RO₂. [HO₂] and [RO₂] vary with time, resulting in a change in the distribution of the reaction pathways. Here we took the average weights throughout 61 s of residence time as the result. The uncertainties on the relative weights of the pathways arise from the uncertainties of [HO₂] and the reaction rate constants. The uncertainty of [HO₂] is 37 % based on the uncertainties of P_{H2O2} (10 %), [OH] (10 %), and [H₂O₂] (6 %) in Eq. S9. To conduct the sensitivity simulations, we doubled or halved the reaction rate constants of RO₂ pathway (kRO2), H-shift pathway (kH-shift) and HO₂ pathway (kHO2) in the model. The input of [HO₂] was either increased or reduced by 40 %. Table S6 and S7 show the results of the sensitivity simulations at 30 % and 80 % RH. The relative weights of the HO₂ and RO₂ pathways of MVK-RO₂ are insensitive to the change of the reaction rate constants and [HO₂], with the HO₂ pathway dominating all the time. For MACR-RO₂, the distribution of the reaction pathways is more sensitive to kHO2 than to other factors. For IEPOX-RO₂, the distribution of the reaction pathways is insensitive to kRO2 while sensitive to kHO2 and kH-shift. The relative weights of the reaction pathways do not vary a lot at 30 % and 80 % RH. We calculate the uncertainties for each pathway with the error propagation formula. The uncertainties are added to the manuscript as follows, “24 ± 15 % (24 ± 13 %), 27 ± 11 % (29 ± 12 %), and 49 ± 20 % (49 ± 22 %) of MACR-derived RO₂ would process through the H-shift pathway, the RO₂ pathway, and the

HO₂ pathway at 30 % (80 %) RH, respectively. 60 ± 23 % (63 ± 23 %) and 39 ± 22 % (36 ± 22 %) of β -IEPOX-derived RO₂ would experience H-shift reactions and cross-reactions with HO₂ at 30 % (80 %) RH, with the rest small part undergoes H-shift reactions”. The relevant description is added to the Supplement.

C6: (Sect. 3.4 Line 353–358)

24 ± 15 % (24 ± 13 %), 27 ± 11 % (29 ± 12 %), and 49 ± 20 % (49 ± 22 %) of MACR-derived RO₂ would process through the H-shift pathway, the RO₂ pathway, and the HO₂ pathway at 30 % (80 %) RH, respectively. 60 ± 23 % (63 ± 23 %) and 39 ± 22 % (36 ± 22 %) of β -IEPOX-derived RO₂ would experience H-shift reactions and cross-reactions with HO₂ at 30 % (80 %) RH, with the rest small part undergoes H-shift reactions. For MVK-derived RO₂, reactions with HO₂ are still dominated (>90 %), and insensitive to the changes in the reaction rate constants and HO₂ concentration within the uncertainties.

Table S6. Sensitivity simulations of the reaction pathways of MVK-, MACR- and IEPOX-derived RO₂ at 30 % RH.

Scenarios	MVK-RO ₂		MACR-RO ₂			IEPOX-RO ₂		
	HO ₂	RO ₂	HO ₂	RO ₂	H-shift	HO ₂	RO ₂	H-shift
Base case	0.93	0.07	0.49	0.27	0.24	0.60	0.01	0.39
kRO ₂ *2	0.93	0.07	0.42	0.34	0.24	0.59	0.03	0.39
kRO ₂ /2	0.93	0.07	0.56	0.21	0.24	0.60	0.01	0.39
kH-shift*2	0.93	0.07	0.41	0.27	0.32	0.46	0.01	0.53
kH-shift/2	0.93	0.07	0.56	0.28	0.16	0.73	0.02	0.26
[HO ₂] +40%	0.95	0.05	0.57	0.23	0.20	0.66	0.01	0.33
[HO ₂] –40%	0.89	0.11	0.38	0.32	0.30	0.49	0.02	0.49
kHO ₂ *2	0.93	0.07	0.64	0.20	0.16	0.73	0.01	0.26
kHO ₂ /2	0.93	0.07	0.34	0.34	0.31	0.46	0.02	0.53

Table S7. Sensitivity simulations of the reaction pathways of MVK-, MACR- and IEPOX-derived RO₂ at 80 % RH.

Scenarios	MVK-RO ₂		MACR-RO ₂			IEPOX-RO ₂		
	HO ₂	RO ₂	HO ₂	RO ₂	H-shift	HO ₂	RO ₂	H-shift
Base case	0.93	0.07	0.49	0.29	0.22	0.63	0.01	0.36
kRO ₂ *2	0.93	0.07	0.42	0.36	0.22	0.62	0.03	0.35
kRO ₂ /2	0.93	0.07	0.57	0.21	0.22	0.63	0.01	0.36
kH-shift*2	0.93	0.07	0.41	0.29	0.30	0.49	0.01	0.50
kH-shift/2	0.93	0.07	0.57	0.29	0.14	0.75	0.02	0.23
[HO ₂] +40%	0.93	0.07	0.57	0.25	0.18	0.69	0.01	0.30
[HO ₂] -40%	0.93	0.07	0.38	0.34	0.28	0.52	0.02	0.46
kHO ₂ *2	0.93	0.07	0.64	0.21	0.15	0.76	0.01	0.23
kHO ₂ /2	0.93	0.07	0.34	0.36	0.30	0.49	0.02	0.49

7. Line S12: why kOH, ISO is used here with MACR and MVK as photochemical clock species?

A7: We are sorry that there is an error in Eq. S2. Here k_{OH,ISO} should be replaced by k_{OH,MACR} and k_{OH,MVK}. We have corrected Eq. S2 in the Supplement.

C7: (Supplement Line 14)

$$OH_{exp,add} = \frac{1}{2} \times \left[\frac{1}{k_{OH,MACR}} \times \left(-\ln \frac{[MACR]_t}{[MACR]_{t0}} \right) + \frac{1}{k_{OH,MVK}} \times \left(-\ln \frac{[MVK]_t}{[MVK]_{t0}} \right) \right] \quad (S2)$$

8. Table S3: how was the UV flux at 254 nm obtained? I find it too small to generate OH exposure >1e11 molec cm⁻³ s with O₃ < 1 ppm. What are the references for the quantum yields reported here? 0.05 for MACR seems to be too low given energetic 254 nm photons.

A8: We applied a box model constrained by the initial and final O₃ concentrations in the OFR at 30% RH to obtain the photolysis rate constant of O₃. Table S5 lists the relevant reactions and their rate constants in the model. The UV flux at 254 nm was obtained by dividing the photolysis rate constant of O₃ by its absorption cross-section and quantum yield at 254 nm. The photolysis of peroxides regenerates OH radicals. Moreover, OH radicals are byproducts of the reactions of ISOPOO and HO₂. These reactions may lead to higher OH exposure than O₃ photolysis alone.

The relevant discussions have been added to the Supplement. The quantum yields reported here are abstracted from MCM v3.3.1 website (<http://mcm.york.ac.uk/home.htm>, last access: 6 October 2022). We have checked their values in Table S3.

C8: (Supplement Line 10–12)

The regeneration of OH from the photolysis of peroxides and the reactions of ISOPOO and HO₂ possibly leads to higher OH exposure than expected from O₃ photolysis alone.

(Supplement Line 29–34)

We applied a box model constrained by the initial and final O₃ concentrations in the OFR at 30 % RH to obtain the photolysis rate constant of O₃. The relevant reactions and their rate constants in the model are listed in Table S5. The UV flux at 254 nm was obtained by dividing the photolysis rate constant of O₃ by its absorption cross-section and quantum yield at 254 nm. $k_{\text{PH},i}$ for the concerned products were obtained by multiplying the photon flux, absorption cross-section and quantum yield at 254 nm.

Table S3: First-order photolysis rate constants ($k_{PH,i}$) of the concerned products in the OFR. The quantum yields and absorption cross-sections are abstracted from MCM v3.3.1 website (<http://mcm.york.ac.uk/home.htm>, last access: 6 October 2022).

Table S5: List of reactions and their rate constants (298 K, 1 atm, 30 % RH) in the model for obtaining the photolysis rate constant of O_3 .

#	Reactions	Rate constants	References
1	$O_3 \rightarrow O^1D$	$1.62D-2^a$	
2	$O_3 \rightarrow O$	$1.80D-3^a$	
3	$O^1D + H_2O \rightarrow OH + OH$	$2.14D-10$	b
4	$O^1D \rightarrow O$	$2.07D+8$	b
5	$O + O_3 \rightarrow$	$7.99D-15$	b
6	$O \rightarrow O_3$	$1.63D+4$	b
7	$HO_2 + HO_2 \rightarrow H_2O_2$	$4.40D-12$	b
8	$HO_2 + OH \rightarrow H_2O$	$1.11D-10$	b
9	$O_3 + OH \rightarrow HO_2$	$7.26D-14$	b
10	$H_2O_2 + OH \rightarrow HO_2 + H_2O$	$1.70D-12$	b
11	$O_3 + HO_2 \rightarrow OH$	$2.02D-15$	b
12	$OH + OH \rightarrow H_2O_2$	$2.60D-11$	c
13	$H_2O_2 \rightarrow OH + OH$	$1.06D-4^d$	

Note: a, adjusted to make the modeled final O_3 concentration meet with the initial one, the quantum yields for O^1D and O are 0.9 and 0.1 over 254 nm; b, abstracted from MCM v3.3.1 website (<http://mcm.york.ac.uk/home.htm>, last access: 6 October 2022); c, Li et al. (2015); d, calculated based on the absorption cross-sections of O_3 and H_2O_2 over ~254 nm.

Technical correction:

Grotheer et al., 1985 cited in Line 254 is missing in the reference list.

A: We are sorry to make such a mistake. Grotheer et al., 1985 cited in Line 254 has been added to the reference list.

C: (Line 539–540)

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