

## Comment on acp-2022-444

Anonymous Referee #1

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Referee comment on "Water enhances the formation of fragmentation products via the cross-reactions of RO<sub>2</sub> and HO<sub>2</sub> in the photooxidation of isoprene" by Jiayun Xu et al., Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2022-444-RC1>, 2022

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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-ISOPOO with HO<sub>2</sub> 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 CH<sub>2</sub>OH (+O<sub>2</sub>) → HOCH<sub>2</sub>O + HO<sub>2</sub> → HMHP in the gas phase. Theoretical calculations showed that CH<sub>2</sub>OH and O<sub>2</sub> are too energetic for HOCH<sub>2</sub>O to be stable. Even transient existence of HOCH<sub>2</sub>O in this pathway will also end up with HCHO and HO<sub>2</sub> 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 CH<sub>2</sub>OH+O<sub>2</sub>.

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.

#### Specific comments:

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

Table 1: are the O<sub>3</sub> concentrations reported in this table initial or final concentrations? They are below 1 ppm. With such low O<sub>3</sub> concentrations and relatively high OH exposures reported here, I expect a substantial loss of O<sub>3</sub> in the reactor by photochemistry.

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.

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.

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.

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

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

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 O $_3$  < 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.

Technical correction:

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

References:

Dibble, T. S.: Mechanism and dynamics of the CH<sub>2</sub>OH+O<sub>2</sub> reaction, *Chem. Phys. Lett.*, 355, 193–200, 2002.

Huang, Y., Zhao, R., Charan, S. M., Kenseth, C. M., Zhang, X., and Seinfeld, J. H.: Unified Theory of Vapor-Wall Mass Transport in Teflon-Walled Environmental Chambers, *Environ. Sci. Technol.*, 52, 2134–2142, 2018.

Liu, Y. J., Herdlinger-Blatt, I., McKinney, K. a., and Martin, S. T.: Production of methyl vinyl ketone and methacrolein via the hydroperoxyl pathway of isoprene oxidation, *Atmos. Chem. Phys.*, 13, 5715–5730, 2013.

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Qiu, J., Ishizuka, S., Tonokura, K., Colussi, A. J., and Enami, S.: Water Dramatically Accelerates the Decomposition of  $\alpha$ -Hydroxyalkyl-Hydroperoxides in Aerosol Particles, *J. Phys. Chem. Lett.*, 10, 5748–5755, 2019.