

Response to the comments by referee #1

We thank the reviewer for the comments.

Comment: Discrepancies between modelled and measured HO₂ concentration in the experiments

Aren't the self-reactions of the nitrated RO₂ the main source for HO₂ in the experiments? According to the discussion on p. 17, the rate coefficients for these self-reactions do not seem to be well established: those reported from the experiments of Schwantes et al. (2015) are significantly different from those used in models.

Would it be possible to adapt the values for these rate coefficients in the model in order to reproduce the observed levels of HO₂?

Response: Subsequent reactions of alkoxy radicals are the main source of HO₂. They are also produced from RO₂ self-reactions as mentioned by the reviewer. However, in the Caltech and FZJ-NO₃ mechanisms alkoxy radicals are also produced from RO₂+HO₂ and RO₂+NO₃ reactions. One of the results of the experiments in our study is that there is a large uncertainty in the yield and the exact fate of alkoxy radicals. Several yields and/or reaction rate constants in the mechanism could be tuned to increase the HO₂ levels (or concentration). Without further experimental hints for example by measured products concentrations, as stated in our conclusion, we do not believe that adapting the RO₂+RO₂ reaction rate constant can be justified as the one solution to achieve a better model-measurement agreement for HO₂ radicals..

Comment: Detection of NISOPOOH vs epoxides with VOCUS

I do not agree with the authors' response concerning the detection of hydroperoxides with VOCUS (or lack thereof) reported by Li et al., 2022. This previous paper clearly reports that no ROOH can be detected by VOCUS, as underlined in their conclusion "(for) ROOH hydroperoxides, (we find) that most of these molecules were also expected to fragment nearly to 100 % under the conditions of the Vocus PTR". This would be interesting to confirm with a standard ROOH compound with the VOCUS instrument used in the present study.

In any case, this is good news for the present study as this strongly supports the detection of epoxides in the experiments: since the VOCUS cannot detect any ROOH, the signals observed at the ion mass for NISOPOOH can certainly not be from NISOPOOH itself (or only a minor fraction) and must mostly result from the isomer epoxides. The same is true for all other ion signals corresponding both to hydroperoxides and peroxides.

Response: In Li et al. 2022, there is another statement in their conclusion: "Importantly, our results suggest that the protonation of ROOR and ROOH species does not automatically lead to total fragmentation.... For the Vocus PTR-TOF used in this study, we predict nearly complete fragmentation for almost all studied chemically labile peroxidized species". Our interpretation of this statement is that (1) the operational conditions / settings of the Vocus PTR-TOF needs to be considered and (2) statements about fragmentation refer to the type of ROOH investigated in that study, which does not include nitrate hydroperoxides. We do not know, which fraction of the nitrate hydroperoxides fragment in the Vocus PTR-TOF though we

observe a qualitatively good agreement with measurements by CIMS instruments which are much less affected by fragmentations on the respective mass. Li et al. state that these instruments are more suitable for the detection of hydroperoxides. If all nitrate hydroperoxide fragmented in the Vocus PTR-TOF, the observed high ion mass signal would require that the sensitivity of the Vocus PTR for nitrate epoxide species must be extraordinarily high. In addition, results from chamber experiments, which we performed (unpublished work), focusing on hydroperoxide and epoxide species from isoprene, showed that the sensitivity of a PTR instrument was much lower for epoxides than for hydroperoxides. For these reasons, we believe that it is unlikely that 100% of the nitrate hydroperoxide species fragmented for settings of our Vocus PTR in our experiments.

We added in L 280: "Fragmentation, though, may reduce the sensitivity of the VOCUS PTR-MS for NISOPOOH at the corresponding mass as shown by Li et al. (2022) for other hydroperoxide species."

Comment: Formation of HPALD in the mechanism

The formation of HPALD is an important point of this paper, yet it is not shown in the mechanism of Fig. 6. It would be useful to add it.

Response: HPALD is not produced from the subsequent chemistry of bi-molecular reactions of the β -1,2 nitrate RO₂ isomer shown in Fig. 6, but is the product of the unimolecular H-shift reaction of the Z- δ RO₂ isomers. Therefore, HPALD production cannot easily be integrated in Fig. 6. We show the reaction pathway of the Z- δ RO₂ isomers leading to HPALD in Fig. 3 instead. This figure is also referenced in Section 5.6, where HPALD production is discussed in detail. We therefore think that there is no additional illustration of this reaction pathway needed in the manuscript.

Comment: The first sentence of the introduction, stating that "Isoprene is the most abundant hydrocarbon in the atmosphere". I should think methane is the most abundant one (~ 2 ppm). With concentrations below 10 ppb, isoprene is probably not even the most abundant non-methane hydrocarbon. It is probably better to say "the most largely emitted" or something equivalent.

Response: We changed the wording to: "...the most emitted non-methane hydrocarbon in the atmosphere".

Comment: A few lines below (li. 35/36), the statement that "the primary organic peroxy radicals (RO₂) formed after the OH addition (on isoprene) are unstable". "Unstable" seems inappropriate here. Some of them undergo some rapid reactions or rearrangement, but not even all of them. Perhaps it is better to refine this statement.

Response: We changed the wording to: "... that the primary organic peroxy radicals (RO₂) formed after the OH addition are in a thermal equilibrium with the alkyl radical through oxygen elimination and re-addition reactions at a time scale ..."

Comment: A few lines below (li. 38/40) the statement that “fast H-shift reactions of minor RO₂ isomers can constitute a large loss process for the entire RO₂ pool” is contradictory in itself. If I understand correctly, the main point here is that the different RO₂ isomers produced by the first addition steps re-arrange between each other (I guess this is what “equilibrate” means in this discussion) so that, rapidly, the proportion between them are not necessarily those expected from the selectivity of the initial addition. In other words, some RO₂ expected to be produced in “minor” fraction by the initial step do not necessarily stay “minor”.

Response: The different RO₂ isomers are in a thermal equilibrium and the equilibrium concentrations for the Z- δ RO₂ isomers are lowest (“minor”) among the 3 RO₂ isomers that are part of the equilibrium. From this, one needs to distinguish the RO₂ loss rate, which can be fast for the unimolecular reaction of this specific Z- δ RO₂ isomer, much faster than the loss in bi-molecular reaction that apply to all RO₂ isomers. To avoid the confusion, we removed the word “minor”.

Comment: As mentioned above, a few sentences might need some further simplification/clarification. I will just mention one example here: In section 4. Results, p. 15 li. 277/278: “The signal can include nitrate epoxides that are produced from the ring-closure reactions of alkoxy radicals (Section 5.3) and the reaction of NISOPOOH with OH, which have the same mass. However, their contribution is expected to be low for most of the time in the experiments in this work...”.

First, it seems that the word “product” is missing between “the reaction” and “NISOPOOH with OH” since a reaction in itself does not have a mass. Or do you mean that different isomers of nitrate epoxides can be produced both from the ring-closure of alkoxy radicals and by the reaction of NISOPOOH with OH? The meaning is somewhat different and, in the later case, “from” should be added in front of “the reaction of NISOPOOH” to clarify. Second, what does “their” refer to ? All the nitrate epoxides produced by both pathways? Or just those produced by the reaction of NISOPOOH with OH... ? Finally the last part of the sentence needs simplifying “However their contribution is expected to be low is most of the experiments in this work...”

I guess you see my point. There are quite a few other sentences in the text that would require similar attention.

Response: We replaced the last part of the sentence “..., which have the same mass.” with “... and from the reaction of NISOPOOH with OH”. As suggested by the reviewer we removed “for most of the time”. We further rephrased: “However, the contribution of nitrate epoxides from the ring-closure reactions to the sum of product concentrations from both reactions is expected”.

We checked the entire manuscript and improved similar sentences.

Response to the comments by referee #2

We thank the reviewer for the comments.

Comment: I still think some of the sections are substantially longer and more complicated/detailed than they need to be, and I encourage the authors to tighten the manuscript further (especially sections 5.7, 6, and 7).

Response: We tightened the manuscript further.

Comment: Figure 3: the second column of yields should perhaps be scaled to those in the first column, so that the percentages sum to 100%, and the values give a sense of the overall RO₂ distribution.

Response: Numbers were changed according to the suggestion of the reviewer.

Comment: Line 226: The possible formation of ROOR should be at least mentioned here. This was a major finding in Ng et al. 2008 but isn't discussed here.

Response: Ng et al. 2008 investigated the production of SOA from the oxidation of isoprene with NO₃. As the authors discuss in their work the yield of ROOR is small for the gas-phase RO₂+RO₂ reaction and only becomes important for SOA formation. In our work, we only discuss major gas-phase reactions. We added in Line 232: "The yield of ROOR compounds from the gas-phase reaction of RO₂+RO₂ radicals is expected to be small. Due to their low volatility, however, ROOR compounds are important for the formation of SOA (Ng et al., 2008)."

Comment: Line 245: The fact that in Figs 4 and 5 concentrations of uncalibrated species are scaled to the predictions of the FZJ model needs to be mentioned in the text, not just the figure caption.

Response: We added in Line 249: "In all figures, ion mass signals of the VOCUS PTR-MS instrument for which no calibration was available were scaled to concentrations predicted by the FZJ-NO₃ model."

Comment: Line 254, 506: Given the importance of HO₂ for all observed and modeled chemistry, there needs to be some discussion of what might cause this model-measurement discrepancy, and what it implies for the present work. I know the discrepancy was discussed in Vereecken et al 2021, but it's too large a difference to simply gloss over in the present work. Might the discrepancy indicate a shortcoming of the organic chemistry simulated in the mechanism?

Response: In the section "Results" we feel that results are sufficiently described (L 254) and all discussion about the model-measurement discrepancy should be in the section "Discussion". Similarly, we feel that the impact of the discrepancy on OH radicals is sufficiently

discussed in L 506. In addition, we discuss the impact on the lifetime / fate of RO₂ radicals in Section 5.2 and give detailed numbers in the Appendix (Figure A4). This is also part of the discussion of the nitrate RO₂ with HO₂ (Section 5.5, L499). We therefore think that the impact of the model-measurement discrepancy for HO₂ on the results of our work is discussed at all relevant points in the section “Discussion”. We do not have a final explanation for the discrepancy. The possibility of a measurement artefact is mentioned in L254. As also mentioned in L254 and L506, there are hints from the OH measurements that at least not all of the discrepancy is likely due to a measurement artefact (L 506). Therefore, a shortcoming of the organic chemistry could also be the reason. However, there is no clear hint from measurement results, which exact reactions may produce additional HO₂.

We added in the section “Conclusion” L. 845: “The large model-measurement discrepancy of HO₂ concentrations hints that HO₂ production in the NO₃+isoprene chemistry is still not well described by the FZJ-NO₃ model (Vereecken et al., 2021).”

Comment: Line 304: throughout, the addition of reaction numbers is very helpful; reaction R14 should be mentioned here.

Response: We added the reaction number “R14”.

Comment: Line 438: “calculated” -> “predicted” or “modelled”

Response: We changed “calculated” to “predicted”.

Comment: Line 462: this repeats something that was states previously (lines 302-304).

Response: We removed this paragraph to avoid the repetition.

Comment: Line 619: This sentence is unclear as written. I think the point is that the loss rate in the MCM is higher than what is observed.

Response: We changed the sentence to: “In contrast, the reaction rate constant implemented in the MCM leads to a loss rate that is too high to be consistent with the observed ion mass signal.”

Comment: Line 668: NO₃ reactivity receives almost no attention here (other than a short paragraph at the end, which mostly references another paper) so shouldn’t be included in the section title.

Response: We think that both OH and NO₃ reactivity measurements give important information about the further oxidation of oxidation products during the night and support what is discussed in Section 5.7. While we recognize that NO₃ reactivity is only discussed briefly, we prefer to also mention it in the heading, so that the reader can locate the section and find the appropriate reference.

Comment: Line 675: Does this take dilution losses into account?

Response: All calculations take dilution into account as explained in the “Methods” section.

Comment: Line 805: This section is very long, and the main points of the paper are often hard to glean. I’d recommend shortening it substantially, and perhaps using bullet points to list the main results as well as potential unknowns / future work.

Response: We shortened the conclusion further by removing 3 paragraphs which might have appeared as repetitive. We prefer to avoid a list of bullet points as we feel that we might lose too much information.

Comment: Line 878: Claiming one mechanism is “valid” seems too strong (as well as subjective), given all the uncertainties and limitations of all complex mechanisms. I would recommend rewording this to highlight which aspects of the chemistry are described more accurately by the FZJ mechanism.

Response: We changed the statement to: “... gives a more complete and accurate description of the nocturnal oxidation of isoprene than previous chemical mechanisms.”

Comment: Typos/grammar: Line 66 (and elsewhere): “only” should go after “included”, to denote that this is the only mechanism that does this (and not that this is the only thing that the mechanism does); 395 (“mechanisms”); 590 (missing an “of”); 797 (“transport”)

Response: Typos are corrected in the revised version.