

We thank the anonymous referees for reading the paper carefully and providing thoughtful comments, which have resulted in improvements in the revised version of the manuscript. We reply to each comment below in bold text.

Anonymous Referee #1

General comments

This paper presents an experimental investigation of the OH-initiated oxidation of isoprene under atmospherically relevant conditions in the SAPHIR chamber. The main focus of the study is the important subset of the chemistry, usually referred to as the Leuven Isoprene Mechanism (LIM1: Peeters et al., 2014), involving the reversible addition of O₂ to OH-isoprene adducts, and the unimolecular isomerisation reactions of a subset of the isomeric HO-isoprene-O₂ peroxy radicals formed. These provide direct regeneration routes for HO_x radicals (OH and HO₂), which are of particular significance at NO_x levels that are characteristic of the remote pristine boundary layer. The experimental observations of the concentrations/mixing ratios of a number of species (OH, HO₂, RO₂, CO and the sum of methylvinyl ketone, methacrolein and isoprene

hydroxyhydroperoxides), and the OH reactivity, are used to test the rate parameter values currently applied to the LIM1 chemistry in the Master Chemical Mechanism (MCM v3.3.1: Jenkin et al., 2015) and the Caltech explicit isoprene mechanism (Wennberg et al., 2018), and adjustments are recommended that allow the model-measurement agreement to be optimised.

The chemistry of the two di-hydroperoxy carbonyl peroxy radicals (di-HPCARP-RO₂) is given some consideration, these being formed in the LIM1 mechanism from the 1,6-H shift reactions of the Z-1,4- and Z-4,1 HO-isoprene-O₂ peroxy radical isomers. The results of theoretical studies for di-HPCARP-RO₂-I (formed from the 1,4- branch) are presented. These allow full elucidation of the detailed chemistry, with the overall effect being confirmed as dominant formation of OH, CO and the corresponding di-hydroperoxy carbonyl product (DHP-MVK) under relevant atmospheric conditions. This has essentially the same effect under relevant conditions as existing more simplified representations (e.g. as in MCM v3.3.1), although the precise mechanism differs. However, the chemistry for di-HPCARP-RO₂-II (formed from the 4,1- branch) remains unresolved, with further study required for the subsequently-formed tri-hydroperoxy acyl radical.

This is an important and informative piece of work, providing new experimental information to test and help optimise current understanding of atmospheric isoprene degradation chemistry under relevant conditions, with some new insights from theoretical studies also being presented. It is therefore appropriate for publication in ACP. However, a number of comments are given below which the authors should consider and address in producing a revised version of the manuscript.

Specific comments

1) The LIM1 mechanism: Because the main focus of the work is the LIM1 mechanism, more information and background should be given to the origin of the parameter choices applied by the developers of MCM v3.3.1 and the Caltech mechanism (i.e. as represented in run M1), and their overall effect characterised as a phenomenological or “bulk” isomerisation rate for the important 1,6 H shift reactions. Specifically, the following points should be considered:

Line 57: In the discussion of the factor of 5 adjustment to the rate coefficients applied to the reversible addition reactions of O₂ to OH-isoprene adducts in MCM v3.3.1, it could be pointed out that this was following a review recommendation by a LIM1 author (Peeters, 2015), informed by preliminary Caltech results (Crouse et al., 2014). As written, this comes across as an arbitrary unsupported assumption, with its origin unexplained. In the ensuing description, it could also be pointed out that the systematic differences applied to the reversible HO-isoprene + O₂ rate coefficients and the Z-delta-RO₂

isomerisation rates in MCM v3.3.1 are related, the latter being optimised so that the phenomenological bulk isomerisation rate matches reported experimental data for HPALD formation (Crouse et al., 2011). Again, this was partly based on the review recommendation of Peeters (2015).

The authors acknowledge the suggestion of the referee and added the motivation for the change as well as the references to the comment and the preliminary results from Caltech.

The following sentences were included in the revised manuscript:

“...This change was prompted by preliminary results from Caltech (Crouse J. D., 2014) and the review by one of the LIM1 authors (Peeters, 2015)...”

“...This change was suggested by one of the LIM1 authors (Peeters, 2015) to maintain the phenomenological bulk isomerization rate in agreement with previous experimental results on hydroperoxy aldehyde (HAPLD) formation (Crouse et al., 2011)...”

Line 59: The description of the rate coefficients applied to the reversible addition reactions of O₂ to OH-isoprene adducts in the Caltech mechanism (as applied in run M1) is also a bit weak. Rather than Wennberg et al. (2018) simply “suggesting” use of the Teng et al. (2017) values, a statement something like “Wennberg et al. (2018) applied their experimentally determined/optimised parameters, as reported by Teng et al. (2017)” would seem more appropriate and accurate. If possible, it would also be useful to include a qualitative statement about the relative magnitude of the Teng et al. (2017) and LIM1 parameters, to help the reader place them relative to the MCM v3.3.1 values. This is not provided in Table 2, and is not easy judge from the information in the supplement.

The sentence as suggested by the referee was added to the revised manuscript. Table 1 includes a full list of the reversible O₂ reactions, so the readers can compare all models discussed in detail. The text now also contains a statement that the rate coefficient differences are up to a factor of 35, which, combined with the updated text and the table, should give the authors a clear idea of the relative values.

As above for MCM v3.3.1, it would also be helpful if some information was given for the Caltech mechanism on the overall effect of the parameters for the HO-isoprene + O₂ reactions and the Z-delta-RO₂ isomerisation reactions, in terms of a phenomenological bulk isomerisation rate. Given the general close agreement of the MCM v3.3.1 and M1 simulations for almost all conditions, it appears that the two representations probably give very similar bulk isomerisation rates, despite the differences in the parameters applied to the component reactions in the mechanism. This is likely because they are both optimised to similar (Caltech) data for HPALD formation. This would seem to be a really important point to make, because the present study is recommending adjustments to the component parameters that likely give a higher bulk isomerization rate and which may therefore not be consistent with the Caltech results.

The phenomenological bulk isomerization rate for each model tested in this study was calculated for the condition of the low NO experiment (Figure 4) and the average value was included in table 2 and discussed at the end of section 4.

“...When comparing the phenomenological bulk isomerization rate among the different models tested within this study calculated for the low NO experiment (Table 2) a similar value is observed for both MCMv3.3.1 and M1 models. This is to be expected as both models are optimised to reproduce the phenomenological bulk isomerization rate as measured from the formation rate of HPALD (Crouse et al., 2011). In addition, in a study by Jenkin et al. (2019) MCMv3.3.1 and M1 models are compared for different NO values and show no significant differences, as also observed within this study. On the other hand, the value obtained from this study is in good agreement with the LIM1 theoretical calculations and is needed to bring measurements and model results in agreement. Between these two groups of models, the bulk rate differs by a factor of 3 to 4. ...”

Lines 81, 93 and 356: The authors appear to be overlooking that the 0.4 yield of HPALD adopted by Wennberg et al. (2018) is made up of 0.25 delta-HPALD + 0.15 beta-HPALD, based on Teng et al. (2017), where delta-HPALD is the species being discussed in the present work. Unlike delta-HPALD, the beta-HPALD isomer is not expected to photolyse rapidly because the C=O and C=C bonds are not conjugated.

This will likely delay and reduce OH formation from that portion of the chemistry. This distinction should be discussed in the present work, and its effect should be examined in a sensitivity test.

As shown with M2 in figure 7, the largest majority of OH radicals following the 1,6-H shift originates from the much faster aldehyde-shift and products rather than from δ -HPALD photolysis (70% and 12%, respectively). Given the large uncertainty in the assignment of the β -HPALD as the GC-MS-detected peak from the study by Teng et al. (2017), the large uncertainty on the yields of both di-HPCARP-RO₂ and δ -HPALD and the uncertainty on the following-up chemistry of the β -HPALD, our choice was to keep the mechanisms similar to the MCMv3.3.1. One test run was performed as suggested by the referee with no OH radical expected to be formed from the β -HPALD as a lower limit case. Less than 5% reduction of OH radicals was observed. In addition, recent theoretical work on photolysis of α -hydroperoxy carbonyls (Liu et al., 2018) suggests that their photolysis rate could be as fast as for δ -HPALD therefore prompting fast OH radical formation.

The presence of two distinct HPALDS as suggested within the Caltech mechanisms together with our reasons for keeping the model similar to both MCMv3.3.1 and LIM1 (with only δ -HPALD) is added to the revised version of the manuscript.

2) Other comments

Line 50: The description of the chemistry presented here only includes the products of OH addition to the terminal carbon atoms in isoprene. Addition to the central carbon atoms is minor, but still significant. For completeness, this should either be described, or some qualification should be included that you are describing only the major addition routes that collectively account for about 90 % of the reaction. It should probably also be pointed out that minor addition to the central carbon atoms is represented in MCMv3.3.1, but excluded in the other sensitivity tests.

The MCMv3.3.1 is the skeleton model for all the sensitivity tests so that the additions to the central carbon are included in all model runs (excluding M0). This has been clarified in the revised version of the manuscript.

Lines 143 and 173: The instrumentation summary is in Table S9 (rather than Table S1), in section E of the supplement. The authors could consider making this more prominent.

The table was added to the main revised manuscript.

Line 165: A single level of HO₂ signal interference from isoprene-derived RO₂ is given. Presumably, this was determined from experiments similar to those reported by Fuchs et al. (2011) for the current configuration, with the RO₂ generated in a calibration radical source from the OH + isoprene reaction in synthetic air. However, the distribution of the isomeric RO₂ radicals in the calibration source likely differs from those in the experiments, because the distribution changes with the rate of competing bimolecular reactions (as first pointed out by Peeters et al., 2014). The distribution will also vary over the ranges of [NO] and temperature that are considered in the experimental studies. Although all the RO₂ isomers form RO that decompose, was any consideration given to possible differences in interference between the different isomers, and any systematic variation that might occur with experimental conditions?

This issue was considered in some detail. Across the conditions in the experiments, the RO₂ speciation does not change overly dramatically, being bracketed between the nascent and the equilibrium populations, without reaching the latter. As noted by the referee, all alkoxy radicals formed in the measurement cell are decomposing, and the expected variations across the relevant RO populations in overall rate and products are again not extreme. Furthermore, even when changing the modeled interference five-fold (from 0.1 to 0.5), much larger than expected from isomeric redistribution, the difference in the predicted HO₂* model concentration is only 8%, small to negligible compared to the measurement uncertainty. Hence, the RO₂ isomeric population is not a determining factor in the signal interference.

Related to this, all RO₂ formed from OH addition to double bonds are expected to lead to HO₂ interference, e.g. as demonstrated for MVK and MACR by Fuchs et al. (2011). Why were interferences from RO₂ formed from OH + MVK, MACR (and other unsaturated products) not taken into consideration?

The RO₂ interferences from OH + MVK and MACR were also considered and this was clarified in the revised manuscript.

Line 175: Measurements of NO₂ using conventional chemiluminescence analysers are notoriously subject to interferences (e.g. from HONO and PANs). Was this taken into account?

The NO₂ instrument in use at the SAPHIR chamber uses a photolytic converter and not a molybdenum converter where the latter can have large interferences from both HONO and PAN. The instrument in use at SAPHIR was tested for both interferences which were found to be both negligible at the concentrations encountered during the experiments performed.

Line 204: As indicated, the OH + ISOPOOH reactions are believed to regenerate a high yield (> 90%) of OH promptly, and therefore do not count towards the OH reactivity. However, this is also partly the case for other ROOH (e.g. when H abstraction adjacent to an -OOH group occurs). There are many species formed with -OOH substituents C5 during isoprene degradation, and OH can also be regenerated rapidly in selected other cases (e.g. OH + glyoxal). Are these reactions included in the modelled OH reactivity total? If not, it is probably an upper limit.

The reaction of isopoohs with OH regenerates OH radical fast enough so that the OH reactivity measurement has to be corrected for it. This was observed with the LP-LIF instrument in use at the SAPHIR chamber during specific isopooH experiments and for completeness it was included in this study. Still, despite the relative large concentration of isopooH expected at the condition of the experiments, the change in reactivity was at max 7%. Other reactions were not included as the uncertainty on the predicted concentrations together with the uncertainty on the efficiency in OH regenerations (as these species were not directly tested within the instrument) will not bring any improvement in the results of the study.

Line 343: The concentration of MVK + MACR + ISOPOOH is also influenced by the removal rates of these species (i.e. not only by the processes of specific interest to the current study). Whereas the removal reaction rate coefficients for MVK and MACR are well studied, those for ISOPOOH are likely subject to some uncertainty. Have uncertainties on other processes (e.g. OH + ISOPOOH) been considered that could help reconcile model-measurement differences?

The contribution of the modelled ISOPOOHs to the sum of MVK+MACR+ISOPOOH measured signal is, at max, 10%. A test run with a factor of 10 faster rate coefficient for the reaction of ISOPOOHs and OH radical decreased the modelled sum of MVK+MACR+ISOPOOH within the

MCMv3.3.1 model by only 7% with no change in the modelled results for the species investigated in this study. Therefore we feel that the inaccurate distribution of the isoprene-RO₂ conformers the MCMv3.3.1 and M1 models is the main cause for the disagreement between model results and observations.

General comment: Some of the parameter choices made in the previous mechanisms have been influenced by the requirement to take account of reported MVK/MACR ratios in addition to many other reported observables. The reported measurements in the present study quantify the sum of the two isomeric species (plus interference from ISOPOOH), and therefore the discussion focuses on the ability of the mechanisms to recreate that lumped observable. It would be useful if the authors also demonstrated how well the preferred optimised parameters recreate reported MVK/MACR ratios, and other observables, e.g. Caltech HPALD production rates referred to above. In this latter case, might this help with drawing conclusions about the HPALD vs. di-HPCARP-RO₂ yields?

As stated in the paper, the MVK and MACR data in our study is uncertain due to the ISOPOOH interference on the measurements, making the MVK/MACR ratio less reliable for a direct numerical intercomparison. Most of the experimental data (see table 7 in Wennberg et al. (2018)) was obtained at high NO, where the MVK/MACR ratio is determined predominantly by the initial OH and O₂ addition site-specificity, and are thus of less interest for the current investigation. Our model predicts a small increase (12%) in the MVK to MACR ratio when going from high NO (~ 1 ppbv) to low NO (0.2 ppbv) conditions; comparing this to figure 4 in the study by Jenkin et al. (2015) suggests we are in the flat section of the MVK/MACR curve. The phenomenological bulk isomerization rate obtained for the low NO condition of our study is faster than what obtained from the MCMv3.3.1 and Caltech model runs (see table 2 in the main paper); these latter models were optimized to the HPALD formation rate obtained from the study by Crouse et al. (2011). It is difficult to compare the bulk rate from our model with the study by Crouse et al. (2011) as the conditions of the experiments (NO and radical concentrations) are not known to us, and might differ from our conditions. Still, given that the MCM/Caltech mechanisms were optimized to Crouse et al. (2011), it is reasonable to assume that the bulk rate obtained from our optimized model for the Crouse et al. conditions will likewise be larger than those in the MCM/Caltech mechanisms. There is however no obvious reason why the two experimental studies (this work; Crouse et al. (2011)) would be in disagreement, and any difference in model prediction of our model compared to MCM/Caltech is thus related to the already presented evidences in our study showing that the latter models do not represent correctly the measured species. Our bulk rate coefficient on the other hand are very similar to the LIM1 data (see table 2 in the main paper), and we see overall an extremely good agreement (see figures S5 in the SI) between these two models, suggesting that we would obtain a similar MVK/MACR ratio across a wider NO range. The very good agreement between the M2 model and LIM1 was underlined in the conclusion of the manuscript.

Lines 294-309: Although full characterisation of the chemistry of di-HPCARP-RO₂-II and the subsequently-formed tri-hydroperoxy acyl radical is beyond the scope of the present work, can the authors provide any interim guidance to mechanism developers here? In the absence of this, I suspect formation of OH, CO and DHP-MACR will necessarily be assumed.

Related to this, line 213 states “The chemistry of di-HPCARP-RO₂ as investigated within this study was implemented in the model”. What was applied in the case of di-HPCARP-RO₂-II?

The theoretical estimate for di-HPCARP-RO₂-II, based on di-HPCARP-RO₂-I theoretical calculations and literature data, indicates competition between CO elimination and O₂ addition. To keep the mechanism manageable in size, and to avoid introducing too much unproven chemistry,

we opted to implement di-HPCARP-RO2-II subsequent chemistry the same as for di-HPCARP-RO2-I, i.e. only decomposition by CO elimination, leading to formation of OH, CO, and DHP-MACR. One should bear in mind that the acylperoxy channel could later be shown to be more important, but unfortunately our experiments are not sensitive to the branching ratio, and additional theoretical calculation and experiments are needed to resolve this issue.

Line 394: As indicated, the modelled RE is a lower limit because not all possible processes are included in the total. Looking at Fig. 11 in Jenkin et al. (2015), and because the MCM v3.3.1 reaction scheme is being used, it might be possible to include one or two more that may contribute to the small shortfall at low NO_x, namely (i) the higher-generation 1,4 H shift isomerisation reactions (e.g. from MACRO2) and (ii) the RC(O)O₂ + HO₂ = RC(O)O + OH + O₂ reactions.

The higher-generation 1,4-H shift isomerization reaction from MACRO2 is already included in the aldehyde-H shift label (Table S6). This has been clarified in the revised manuscript. There are a large number of additional reactions which also contribute to the OH radical regeneration and which are not included (e.g. fast decomposition of RO₂) as the purpose is to focus on the main regeneration paths which, alone, can more or less explain the observations.

Abstract, Line 19: The effect of temperature over the range 25-41 C is not at all apparent in the discussion of the results. Indeed, I do not think temperature is mentioned again in relation to the experimental study and its interpretation (i.e. it is only mentioned in relation to the model set-up and the theoretical calculations).

The referee is correct and the remark in the abstract was removed.

Minor comments

First two sentences of abstract: The terms "previously" and "early" used here are very vague. Presumably, "previously" means prior to Peeters et al. (2009) (rather than prior to the present work), and "early" means Lelieveld et al. (2008).

The sentence was rephrased.

Line 210: Should "methoxy" should be "methyl peroxy, CH₃O₂"?

Yes.

Line 397: It would be clearer to use a multiplication sign rather than "x" in Eq. (2), particularly as one of the variables is a lower case "y".

Done.

Line 541: The modelled/measured ratio given for the sum of MVK, MACR and ISOPOOH appears to be measured/modelled.

Yes, it was corrected accordingly.

Supplement: The red text is apparently missing in Table S2.

It was added in the revised version.

Anonymous Referee #2

This publication presents a set of chamber studies carried out under representative ambient atmospheric conditions in the outdoor SAPHIR chamber on the photooxidation of isoprene. A comprehensive set of measurements (including radicals HO_x and RO_x) were made over a range of VOC/NO_x conditions, so that the sensitivity of “low-NO” peroxy radical isomerization reactions and subsequent radical regeneration chemistry can be mapped out in order to evaluate the detailed isoprene degradation chemistry described in the detailed MCMv3.3.1 and Caltech isoprene mechanisms. The chamber measurements and modelling were supported by detailed theoretical calculations focusing on the chemistry of the di-HCARP-RO₂ species. The experimental and theoretical work here have been used to recommend updates to the chemistry in both mechanisms and highlight where further research into the low NO isoprene chemical mechanism (i.e. HPALD vs. diHCARP yields and further chemistry) needs to be focused.

This is an interesting and valuable detailed study into the sensitivity of isoprene photooxidation chemistry over a range of NO_x conditions, under atmospherically relevant conditions, providing an important dataset with which to evaluate and optimise our current mechanistic understanding of the atmospheric chemistry, providing future focus in which the chemical uncertainties lie. The manuscript is generally written well, with a few spelling and grammatical errors which need to be fixed. I recommend publication in ACP after the following points are addressed.

I agree with the anonymous Referee #1 that more detail on the development of the MCMv3.3.1 and Caltech isoprene chemical mechanisms need to be brought out in the introduction and place into context of how the developments of these schemes stem from the original LIM1 mechanism, with the further developments of the chemistry applied so that they fit a range of atmospheric conditions. For example, the development of the MCMv3.3 to MCMv3.3.1 comes from detailed discussions between the MCM and LIM1 development teams, using the latest experimental data at the time to scale various rate constants that a very pertinent to the current study (i.e. why the equilibrium rate constants between the isoprene - RO₂ species are increased by a factor of 5 (Line 57) and why the 1,6-H shift RO₂ isomerisation rates are reduced by a factor of 5 (Line 67)). Much of this developmental discussions is given in the ACPD responses section (<https://www.atmos-chemphys.net/15/11433/2015/acp-15-11433-2015-discussion.html>), and should be referenced appropriately. One more thing to note is that the MCMv3.3.1 and the main updates to the Caltech isoprene mechanism (including evaluated in the kinetics and products of 1,6 H-shift reactions of Z- δ -hydroxy peroxy isomers and of first-generation β -hydroxy peroxy isomer + HO₂ reactions) have been evaluated over a range of NO_x conditions in Jenkin et al., (2019) (<https://doi.org/10.1016/j.atmosenv.2019.05.055>), showing some differences in the HPALD and di-HCARP-RO₂ formation, as well as RONO₂ formation, with general agreement over the different NO ranges looked at deemed acceptable.

The reference to the comment by one of the author of LIM1 (Peeters, 2015) to the MCMv3.3 manuscript was added to the introduction of the paper together with the reasoning behind the choices made (please refer to the answer to the first comment of Referee #1).

The reference to the study comparing the MCMv3.3.1 and the updated Caltech mechanisms was added to the end of section 4.

“...In addition, in a study by Jenkin et al. (2019) MCMv3.3.1 and M1 models are compared for different NO values and show no significant differences, as also observed within this study...”

In the **Model Calculations** section, add at line 182 that “... with newly updated isoprene chemistry in line with LIM1 chemistry, updated/optimised to recent experimental results, as described in Jenkin et al., (2015)”

Done

Line 330. The statement about an overprediction of ISOPOOH is not backed up by the measurements here, unless you can estimate the relative fractions of MACR, MVK and ISOPOOH that make up the mass signal in the PTR.

The sentence was removed and rephrased later in the section to underline how the MCMv3.3.1 and M1 models, by having a different distribution of isoprene-RO₂ conformers, predict a larger concentration of ISOPOOH compared to the model M2.

“...In addition, both MCMv3.3.1 and M1 models predict a larger concentration of ISOPOOHs compared to the optimized model M2 due to the different distribution of isoprene-RO₂ conformers. This will cause a larger expected concentration of new particle formed during the oxidation of isoprene due to the subsequent degradation products of ISOPOOHs which includes epoxides (St. Clair et al., 2016)...”

Line 379. Consider putting the additional model run described here in the Supplementary

A figure containing M2, M3 and LIM1 was added to the supporting information (Fig. S5).

Line 455. So the additional global model run includes M3 chemistry?

That is correct and it was clarified in the revised version of the manuscript.

Figure 5. Consider adding the MCMv3.3.1 model simulation to Figure 5, for a direct comparison with Figure 4.

The MCMv3.3.1 model was added to Figure 5.

The **Supplementary Material** pdf consists of 1074 pages!! The majority of this consists of the raw quantum chemical and theoretical kinetic database. Please place this information into an online data store (github) or a supplementary zip files as this data (all though important) is only really relevant/useful to specialist QM chemists.

As suggested, the raw quantum chemical and theoretical kinetics data will be separated from the supporting information and provided as a supplementary zip file. We prefer not to put the data in a separate data repository as it is not too large, and can thus easily be kept together.

Minor Comments

- Abstract – is “disregarded” the right word here? I would use “unrecognised” or “undiscovered” here, or re-write the sentence to say that they were previously not thought to be important under atmospheric conditions...

Changed as suggested.

- Define “parts per billion” earlier, when first used

Done.

- Line 27 - “aldehydic hydrogen”

Done.

- Throughout the main text and supplementary, please refer to “**MCMv3.3.1**” and not “**MCM 331**”.

Done.

- Line 165 – define “ROx”

Done.

- Line 210 – “{10 % methyl peroxy radical and 30% RO₂ radicals from isoprene}”- give a reference for these numbers

Done.

- Line 216 – Link bullet points to Table 2 or expand into a better version of Table 2

Done.

- Line 235 -Link changes to the isoprene chemistry to Table S7

Done.

- Should “DHP-MVK” be “DHP-MEK” throughout the manuscript (Figures 2 and 3)?

The authors decided to use the name as in use in the study by Wennberg et al. (2018) as MVK is formed from the OH addition to C1.

- Line 557. Define OH additions on C4 and C1 – “radical formed from initial OH attack at the C4 and C1 positions...”

The reference to figure 1 was added.

References

Crouse J. D., A. T., P. O. Wennberg: Experimental constraints on the distribution and fate of peroxy radicals formed in the reactions of isoprene + OH + O₂ presented at the Atmospheric Chemical Mechanisms: Simple Models - Real world Complexities, University of California, Davis, USA, 2014.

Crouse, J. D., Paulot, F., Kjaergaard, H. G., and Wennberg, P. O.: Peroxy radical isomerization in the oxidation of isoprene, *Phys. Chem. Chem. Phys.*, 13, 13607-13613, doi:10.1039/c1cp21330j, 2011.

Jenkin, M. E., Young, J. C., and Rickard, A. R.: The MCM v3.3.1 degradation scheme for isoprene, *Atmos Chem Phys*, 15, 11433-11459, doi:10.5194/acp-15-11433-2015, 2015.

Jenkin, M. E., Khan, M. A. H., Shallcross, D. E., Bergström, R., Simpson, D., Murphy, K. L. C., and Rickard, A. R.: The CRI v2.2 reduced degradation scheme for isoprene, *Atmos Environ*, 212, 172-182, doi:<https://doi.org/10.1016/j.atmosenv.2019.05.055>, 2019.

Liu, Z., Nguyen, V. S., Harvey, J., Muller, J.-F., and Peeters, J.: The photolysis of [small alpha]-hydroperoxycarbonyls, *Phys Chem Chem Phys*, 20, 6970-6979, doi:10.1039/C7CP08421H, 2018.

Peeters, J.: Interactive comment on "The MCM v3.3. degradation scheme for isoprene" by M. E. Jenkin et al., *Atmos Chem Phys Discuss*, 15, 2015.

St. Clair, J. M., Rivera-Rios, J. C., Crouse, J. D., Knap, H. C., Bates, K. H., Teng, A. P., Jørgensen, S., Kjaergaard, H. G., Keutsch, F. N., and Wennberg, P. O.: Kinetics and Products of the Reaction of the First-Generation Isoprene Hydroxy Hydroperoxide (ISOPOOH) with OH, *The Journal of Physical Chemistry A*, 120, 1441-1451, doi:10.1021/acs.jpca.5b06532, 2016.

Teng, A. P., Crouse, J. D., and Wennberg, P. O.: Isoprene peroxy radical dynamics, *J Am Chem Soc*, 139, 5367-5377, doi:10.1021/jacs.6b12838, 2017.

Wennberg, P. O., Bates, K. H., Crouse, J. D., Dodson, L. G., McVay, R. C., Mertens, L. A., Nguyen, T. B., Praske, E., Schwantes, R. H., Smarte, M. D., St Clair, J. M., Teng, A. P., Zhang, X., and Seinfeld, J. H.: Gas-phase reactions of isoprene and its major oxidation products, *Chem. Rev.*, doi:10.1021/acs.chemrev.7b00439, 2018.