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Interactive comment on “Importance of isomerization reactions for the OH radical regeneration from the photo-oxidation of isoprene investigated in the atmospheric simulation chamber SAPHIR” *by* Anna Novelli et al.

Anonymous Referee #2

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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 HOx radicals (OH and HO2), which are of particular signifi-

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cance at NOx 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.

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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 (Crounse 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 (Crounse et al., 2011). Again, this was partly based on the review recommendation of Peeters (2015).

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.

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 isomerisation rate - and which may therefore not be consistent with the Caltech results.

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.

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

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be pointed out that minor addition to the central carbon atoms is represented in MCM v3.3.1, but excluded in the other sensitivity tests.

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.

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?

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?

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?

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 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.

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?

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?

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?

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 NOx, 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.

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).

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).

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

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”.

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

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

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