Atmos. Chem. Phys. Discuss.,
https://doi.org/10.5194/acp-2019-328-RC1, 2019

Atmospheric Chemistry and Physics
Open Access
Discussions

# *Interactive comment on* "A new model mechanism for atmospheric oxidation of isoprene: global effects on oxidants, nitrogen oxides, organic products, and secondary organic aerosol" *by* Kelvin H. Bates and Daniel J. Jacob

**Anonymous Referee #1**

Received and published: 17 May 2019

General comments

This paper presents a detailed assessment of the performance of the Reduced Caltech Isoprene Mechanism (RCIM) of Wennberg et al. (2018) in a series of models (box and GEOS-Chem global 3D), and uses it as a reference to produce a further condensed isoprene mechanism (the Mini-Caltech Isoprene Mechanism, Mini-CIM). Although still containing 108 species participating in 345 reactions, Mini-CIM is comparable in size to the existing GEOS-Chem isoprene mechanism (in GEOS-Chem v11-02c). The comparative performances of the reduced schemes in GEOS-Chem are presented and

discussed, with particular reference to the impacts of the updates on HOx recycling, NOx recycling and the formation of oxygenated products, including SOA precursors.

The performance of RCIM is also compared in detail with the performances of the isoprene chemistry in the Master Chemical Mechanism (MCM v3.3.1) and GEOS-Chem v11-02c in box model simulations. Similarities and differences are discussed in some detail, and related to specific pathways within the oxidation schemes.

This is a comprehensive and informative piece of work. It is important that the treatment of isoprene chemistry in global models reflects the significant developments in understanding that have occurred in recent years. Papers such as this, which aim to transfer the detailed understanding into reduced mechanisms in a transparent way, are therefore essential. This is therefore an important paper, which is appropriate for, and worthy of publication in, ACP. Below are a number of comments which the authors should consider in producing a revised version of the manuscript.

Specific comments

1) RCIM is a condensed version of the comprehensive (explicit) mechanism presented by Wennberg et al. (2018). In a few places, I found that I wanted a little more explanation of the underlying reasons for presented differences in performance of RCIM compared with the detailed MCM scheme, i.e. (i) are they due to different fundamental assumptions in MCM and the Wennberg et al. (2018) comprehensive mechanism; or (ii) do they result from simplifications made in RCIM compared with the Wennberg et al. (2018) comprehensive mechanism? If the former, are the differences because there is currently no experimental information to base the chemistry on, and different assumptions have been made? I think such clarification is necessary, because the differences are being presented as an improvement on former mechanisms (whether intentionally or unintentionally) and it is important for the reader to understand their origin. If based on provisional assumptions or conjecture, highlighting this can help guide future research effort.

Some specific examples are as follows (although I probably could list others):

a) Page 11, glyoxal section: The peak production of glyoxal at low [NO] from RCIM is explained by "….contributions from ISOPOO H-shifts and the degradation of IEPOX", and contrasted with that from MCM. Inspecting Figs. 3 and 8 of Jenkin et al. (2015), it appears that MCM does have routes to glyoxal (and methyl glyoxal) from both ISOPOO 1,6 H-shifts and the degradation of IEPOX, with this chemistry informed by mechanistic information presented by Peeters et al. (2014) and Bates et al. (2014). However, they rely on RO2 to RO conversion and therefore require reaction of RO2 with NO, NO3 or RO2. At low [NO] these processes are generally outrun by competing 1,4 formyl H atom shifts or reaction with HO2.

Wennberg et al. (2018) assume very high propagating channel branching ratios for the reactions of HO2 with RO2 radicals formed from OH + IEPOX, and those formed following the 1,6 ISOPOO H-shifts. These reactions provide additional RO2 to RO conversion routes at low [NO], with associated formation of glyoxal (and methyl glyoxal) and OH. This assumption may or may not prove to be correct, but at present there is no evidence from elementary kinetics studies of RO2 + HO2 reactions to support propagating branching ratios as high as some of those applied.

In the specific cases of the mechanisms following the ISOPOO 1,6 H-shifts, major products in both RCIM and MCM are dihydroperoxy carbonyl products, di-HPCARBs (called DHP-MVK and DHP-MACR by Wennberg et al., 2018), formed from 1,4 formyl H atom shift reactions of intermediate RO2. According to Fig. S4 of Wennberg et al. (2018), rapid exclusive photolysis of di-HPCARBs is assumed (instantaneous in RCIM) leading significantly to methylglyoxal formation, and some glyoxal formation (via HOOCH2CHO) in conjunction with substantial OH formation. Wennberg et al. (2018) indicate that "No experimental evidence exists to constrain these rates and products, so the mechanisms shown here are strictly conjectural". Because the di-HPCARBs do not contain a conjugated C=C double bond, it is likely that their photolysis is not exceptionally rapid, and MCM logically represents competitive loss by reaction with OH. This reduces the yield, and delays formation, of methylglyoxal and glyoxal.

It therefore appears that at least some of the higher formation of glyoxal in RCIM at low [NO] results from assumptions that differ from those in MCM, which may or may not be correct. This therefore highlights areas of uncertainty in understanding, where more information is required, and this should probably be made clearer.

b) Page 8, from line 21: The higher concentrations of OH at low [NO] in RCIM compared with MCM are attributed to "… updated H-shift chemistry in RCIM, which efficiently recycles HOx…" with the ISOPOO 1,6 H-shifts producing "… 2.2 equivalents of HOx (1.5 OH + 0.7 HO2) concurrently with the first generation of stable products".

This is therefore related to the processes summarized above for glyoxal and methylglyoxal, in particular the assumed instantaneous photolysis of the major di-HPCARB products producing substantial OH and some HO2 (Fig. S4 of Wennberg et al., 2018). The competitive removal of di-HPCARBs by reaction with OH in MCM clearly leads to a significant difference in the HOx yield from this branch of the chemistry. As indicated above, Wennberg et al. (2018) also generally assume very high propagating channel branching ratios for the reactions of HO2 with RO2 radicals, which also helps to sustain HOx radical concentrations at low [NO].

It should probably be made clearer that the higher OH at low [NO] in RCIM results at least partly from the assumed choice of processes that maximize HOx regeneration, rather than from recent advances in understanding that are reported in Wennberg et al. (2018) and not considered in earlier mechanisms.

2) Page 5: I generally applaud the use of several modeling approaches, as they can each have advantages and disadvantages. However, the use of the "fixed radical box modeling" method would benefit from further justification of why it is of value. At present, it seems to be justified by the following sentence:

"This method serves to remove most nonlinearities and feedbacks inherent in the isoprene oxidation mechanism, so as to isolate the effects of the radicals on the oxidation pathways."

Surely, the non-linearities and feedbacks (i.e. on HOx and NOx) exemplify the major differences between the mechanisms and contribute to the "effects of the radicals on the oxidation pathways" in the different mechanisms. While I understand that you can look at the OH-initiated oxidation alone (i.e., without O3- and NO3-initiated oxidation), it is quite difficult to understand how heavily constraining the system provides reliable information on comparative mechanism performance.

Page 7, line 21: Related to above, > 10 ppb NO is stated to be "not of general atmospheric relevance". However, the fixed box model outputs in the SI present results and comparisons up to 100 ppb NO, with some of the largest differences occurring between 10 ppb and 100 ppb.

Minor comments

Page 1 line 20: Because simulated [OH] varies by an order of magnitude (e.g. Fig. 5), probably should give corresponding [OH] for the stated lifetime.

Page 2, line 23: I think "Heinz Becker" should simply be "Becker" (i.e. his first name is Karl-Heinz). Similarly in the reference list "Becker, K. H." rather than "Heinz Becker, K."

Page 3, line 1: I believe inclusion of Archibald et al. (2010) reference in this set of references is incorrect, because that study specifically did not consider hypothetical OH recycling mechanisms. In contrast, it systematically considered a series of explicit HOx recycling mechanisms based on reported experimental and theoretical data, and was one of the first (or possibly the first) to support and demonstrate the potential significance of the reversible O2 addition/peroxy radical isomerisation chemistry reported by Peeters et al. (2009), and subsequently characterized in detail by Wennberg and co-workers. The historical overview therefore needs some adjustment, and should also give more recognition to Peeters and co-workers for their pivotal role in moving the

understanding of isoprene chemistry forward.

Page 8, line 24: In relation to HOx production and recycling, the following statement is made about RCIM: "Assuming that photolysis is the dominant fate of the conjugated hydroperoxy-aldehydes (HPALDs) that make up 60% of the stable products, HOx production can increase . . ."

If I understand pp 3352/53 of Wennberg et al. (2018) correctly, the conjugated HPALDs actually only account for 25 % of the products following 1,6 H isomerization; with 15 % unconjugated HPALDs and the remainder other products (e.g. di-HPCARBs). This seems quite different from the stated 60 %. Looking at Fig. 6, it looks like the conjugated species make up 60 % of the total HPALDs, but are 24 % (i.e. 60 % of 40 %) of the full suite of products (with 16 % being the unconjugated species). If this is correct, I presume that the statement on Page 8, line 5 should specify "60% of the HPALDs" rather than "60% of the stable products".

Fig. S4 caption – I think "fun" should be "run".

Fig. S19 caption – I think "Jenkin et al. 2015" here is incorrect.

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