

Interactive comment on “A comparison of chemical mechanisms using Tagged Ozone Production Potential (TOPP) analysis” by J. Coates and T. M. Butler

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The VOC degradation chemistry in a number of atmospheric chemical mechanisms is evaluated in terms of the formation of ozone over a period of several days, with the calculations carried out for idealised atmospheric conditions using the MECCA box model. This work builds upon the previous study of Butler et al. (2011), in which total ozone formation potentials were calculated for a set of 21 emitted VOCs using a detailed tagging approach applied to a subset of the highly explicit Master Chemical Mechanism (MCM) – leading to development of the Tagged Ozone Production Potential (TOPP) concept.

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The present study uses MCM v3.2 (and v3.1) as a reference mechanism against which to evaluate the impacts of a variety of reduction methods, as applied in a number of popular mechanisms, namely: MOZART-4, RADM2, RACM, RACM2, CBM-IV, CB05 and CRI v2. As a highly explicit mechanism, MCM v3.2 has the luxury of being able to apply prevailing understanding of atmospheric chemical processes directly and in great detail, and is therefore the logical choice as a reference mechanism. Mechanism reduction is inevitably a balance between maintaining performance and improving how quickly the mechanism runs in a model. More reduced mechanisms will therefore generally need to compromise performance to some extent, to become more efficient relative to a highly explicit mechanism – with the aim being to minimise the former whilst maximising the latter. The present study examines the impacts of these compromises in a systematic and transparent way, and thus provides valuable information to help guide mechanism developers. Of course, all mechanisms also ideally need to be evaluated against measurement data, as even highly explicit mechanisms are only as good as the prevailing process information they contain.

The authors also sensibly apply a level of “harmonisation” to the chemical mechanisms (e.g. using the same inorganic reaction set with each) to ensure that the differences in performance result from the differences in the way VOC degradation chemistry is represented. The results show enormous variability in the performances of the various reduced mechanisms (even on day 1), clearly demonstrating that reduction methods and assumptions can have a large impact on simulated ozone formation. The larger discrepancies on subsequent days are particularly important for regions such as north-west Europe, where elevated ozone levels are usually associated with multi-day chemistry and transport.

This is a fascinating piece of work, providing valuable guidance to mechanism developers and users. The paper is generally well written, and should be published subject to consideration of the points given below.

1) The study uses a speciation of 20 VOCs, consisting of alkanes, alkenes (including

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isoprene) and aromatic hydrocarbons (with acetylene also previously included by Butler et al., 2011). Given that some inventory speciations contain several hundred VOCs for typical urban sources, it could be argued that this is already a substantially lumped representation – or maybe more correctly an incomplete speciation, as it is based on reported measurements of a subset of species (although probably the generally more important ones). As a result, the reference MCM simulations are themselves already a reduction, using only a subset of the mechanism. The numbers of species and reactions listed for MCM v3.2 and MCM v3.1 (and CRI v2) in Table 1 should therefore probably more correctly correspond to the VOC speciation, as many species in the complete mechanisms are not participating in the chemistry. These can be obtained using the subset mechanism assembling facilities at the relevant MCM and CRI websites (see end of review). If the authors also wish to keep the existing full mechanism numbers, the subset numbers could be included in a footnote.

2) The discussion illustrates many differences in mechanism performance, and the origins of these differences are generally well described and discussed. In some instances, however, the discrepancies are attributed to very specific and precise causes which do not seem fully justified.

For example, on page 12400 (line 12) the high Ox formation from propane degradation in RACM2 is attributed to the mechanism species HC3 producing about 17 times the amount of acetaldehyde that is produced from propane in MCM v3.2. This high ratio arises because acetaldehyde is not a significant first generation product of propane degradation, and therefore not formed in MCM v3.2 until the second-generation chemistry (specifically the further oxidation of the relatively minor product, propanal). Acetaldehyde is therefore formed in RACM2 instead of other products formed in MCM v3.2 (mainly acetone, and some propanal). Acetone, has a low OH reactivity (and photolysis rate) and is not significantly oxidised on the several day timescale of these calculations, thereby largely halting Ox formation after the first-generation chemistry. I suggest it is therefore the failure of RACM2 to represent the high yield of an unreactive

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product that results in its overestimate in Ox. Although the high relative formation of acetaldehyde on day 1 with RACM2 and MCM v3.2 is one consequence of this, it is not itself the source of the Ox overestimate with RACM2.

Another example is on page 12402 (line 28), where the second day maximum in Ox from toluene degradation with RACM2 and CRI v2 is attributed to "...increased C₂H₅O₂ production from degradation of unsaturated dicarbonyls; C₂H₅O₂ is not produced during degradation of unsaturated dicarbonyls in the MCM v3.2."

I am particularly familiar with CRI v2, and I agree that a likely contributor to the discrepancy is that the formation of the (relatively reactive) unsaturated dicarbonyls (UDCARB8 and UDCARB11) is too efficient. C₂H₅O₂ is indeed used as a representative peroxy radical, formed from one channel of the oxidation of UDCARB8 - this being the surrogate for butenedial (MALDIAL) in MCM v3.2. However, MALDIAL is also oxidised to peroxy radicals (MALDIALO₂ and MALDIALCO₃) in MCM v3.2, with the fraction not leading to anhydride formation being represented by C₂H₅O₂ in CRI v2. I therefore do not think this is an unreasonable assignment (note that contributions of MALDIALO₂ + NO and MALDIALCO₃ + NO are probably hidden within the large "production others" category for MCM v3.2). It is more that the formation of the unsaturated dicarbonyls is too efficient in CRI v2, and that their degradation produces Ox, regardless of which peroxy radicals are used as representatives. Although the fluxes through the reactions of NO with the specific peroxy radicals (C₂H₅O₂ from UDCARB8 and RN10O₂ from UDCARB11) are how this is quantified in the present study, I think that highlighting increased production of C₂H₅O₂ as the sole specific cause is not particularly instructive, as it is once again a consequence of the real cause.

Minor comments

General "Volatile organic compounds" seems to be abbreviated as either "VOC" or "VOCs" at different points in the manuscript. Given that the original definition on line 3 of the Introduction is "VOCs", I would suggest using this consistently throughout, unless

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talking about an individual VOC.

Page 12391, line 22: perhaps it should be stated that VOCs are oxidised mainly by reaction with the OH radical, to acknowledge the existence of other initiation pathways.

Page 12392: perhaps it should be clarified that Reaction (R4) specifically illustrates the abstraction of H from a VOC by reaction with OH, as occurs exclusively for alkanes. The main routes for the reactions of OH with alkenes and aromatics proceed by OH addition.

Page 12394, line 13: As stated, the full CRI v2 does lump degradation products into common representatives. Although not used in the present study, its further reduced variants (e.g. CRI v2-R5) also lump emitted VOCs using POCP as a criterion (Watson et al., 2008), so that they are subsets of the full mechanism. As indicated in comment 1 above, the present work also uses a subset of the full mechanism, so I'm not sure that use of the "full CRI" can be claimed on page 12395, line 19.

Page 12398, line 9: The use of a family of Ox species is a sensible approach. However, it might be worth giving a formal definition of "other species involved in fast cycling with NO₂", as those shown have a wide range of cycling lifetimes. Are PANs sufficiently short-lived?

Other comments

3) Page 12395, lines 13-22: MCM v3.2 is used as the reference mechanism in this study, with MCM v3.1 also considered for completeness, because it was the reference for the original development of CRI v2 (Jenkin et al., 2008). Because an overview description of MCM v3.2 has never been published in the open literature, I provide here a short summary of the updates. This is mainly for information, and not necessarily for reproduction in the paper, unless deemed helpful by the authors.

In practice the differences between MCM v3.1 and v3.2 are probably very subtle for the applications presented here. The main updates in MCM v3.2 were:

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(i) The development/inclusion of new schemes for limonene, β -caryophyllene and dimethylsulphide, none of which are used in the present work. Only the β -caryophyllene work has been documented (Jenkin et al., 2012).

(ii) There was also a (now historical) update to the isoprene chemistry, which has been documented along with more recent developments by Jenkin et al. (2015). The update mainly consisted of implementing detailed revised chemistry for isoprene-derived hydroperoxides and nitrates. Based on the comparisons in the present study, these updates only have a minor impact on the simulations for the considered conditions.

(iii) Radical propagating channels were implemented for the reactions of HO₂ with acyl peroxy radicals throughout the mechanism. This potentially influences the chemistry of all the VOCs considered here, although of greater significance at high [VOC]/[NO_x].

(iv) Routine update of rate coefficients to IUPAC recommendations. Any impact of this (which would probably be quite small in any case) will mainly have been eclipsed by the (fully justifiable) mechanism harmonisation measures carried out by the authors.

Because there is no overview publication, the authors have used the citation "Rickard et al. (2015)" for the MCM v3.2 website. I suggest the author list of this citation is expanded to include those listed as "current contributors" on the citation tab of the MCM v3.2 website (<http://mcm.leeds.ac.uk/MCMv3.2/contributors.htm>).

4) I note from the response to another reviewer (Coates and Butler, Atmos. Chem. Phys. Discuss., 15, C3816, 2015) that the authors are proposing to include references to the studies of Bloss et al. (2005) and Pinho et al. (2005) to illustrate that the MCM has had difficulties in reproducing the results of chamber studies for aromatic VOCs and isoprene. Whilst I agree with this for aromatics, the main conclusion of Pinho et al. (2005) was that the MCM v3 isoprene scheme (written in 2001) performed very well. The major factor responsible for deviations in performance of the MCM v3 scheme from the SAPRC chamber data was the absence of the reaction of O(3P) with isoprene in MCM v3, this reaction being insignificant under atmospheric conditions. A number of

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other less important refinements were also identified by Pinho et al. (2005), and these were all implemented long before release of MCM v3.2 in 2011. I therefore think it is misleading to report that the MCM has had difficulties in reproducing the results of traditional chamber studies for isoprene.

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