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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Impacts of mechanistic changes on HO_x formation and recycling in the oxidation of isoprene" *by* A. T. Archibald et al.

A. T. Archibald et al.

atmos.chem@btinternet.com

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We thank referee 1 for providing a review of our paper. We would normally reply to all referees' comments in a single response at the end of the discussion period. However, in view of the general and sustained extreme negativity of this review, we feel it is important to provide a timely series of responses to the comments made. In our opinion, the majority of the points raised by the referee are misleading or incorrect, and generally misrepresent the aims, content and output of the paper.

Ref 1: opening comment:

The manuscript by Archibald et al. describes modeling exercises with the MCM Leeds chemistry mechanism. Newly proposed changes in HOx recycling are incorporated

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and used to derive a simplified representation for increased HOx production in a global model. In it's present form the manuscript lacks experimental data to compare with and poorly reflects observational studies on isoprene chemistry that have been published in the peer reviewed literature. Without inclusion of observational results or a better discussion of the observational literature the manuscript does not contribute any significantly new insights compared to what has already been published on this subject (e.g. Peeters et al., 2009; Paulot et al., 2009; Lelieveld et al., 2008; Butler et al. 2008; Karl et al., 2009; Archibald et al., 2009; Silva et al., ES&T, 2010, Pugh et al., 2010).

Response to opening comment:

The referee's opening two sentences do not accurately describe the scope of the paper. It first presents a detailed and systematic mechanistic sensitivity test, which investigates and discusses the impacts of a series of recently reported and proposed changes to the degradation chemistry of isoprene; with a particular focus on recycling of OH radicals. It then goes on to develop a reduced representation of the chemistry for use in a global CTM, and presents the results of a global simulation using this reduced representation.

The referee goes on to raise two general objections. The first suggests that the paper needs to provide direct comparisons of model output with field observational data to be valid. Although such direct comparisons can be informative, we strongly disagree that that approach is the only valid one – and often it is not the most appropriate for a chemical mechanism sensitivity test. Simulation of field data requires a model which includes an appropriate description of a variety of processes (including correct representation of the strength and temporal variation of emissions, entrainment of background air, and deposition). The scope for systematic and compensating errors, and the desire to "fit" observations, can therefore inhibit a true appraisal of a chemical mechanism. As a result, the systematic testing of chemical mechanisms over a range of conditions using box models is a long-established and informative activity, with numerous papers reported in ACP and elsewhere using this approach (e.g., Poechl et al., 2000; Kuhn

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et al., 1998; Emmerson and Evans, 2009; Archibald et al., 2009). The present work therefore uses an appropriate method to analyse and report the sensitivity of the system to a series of changes to a detailed reference mechanism over a wide range of atmospherically-relevant conditions.

In practice (and as outlined in the introduction to the paper), there is a clearly-defined link to reported model-measurement discrepancies in the field, via the studies of Lelieveld et al. (2008), Butler et al. (2008) and Kubistin et al. (2008). Those studies reported that it was impossible to reconcile model output and measurements of OH radical concentrations in isoprene-dominated locations using the prevailing understanding of isoprene chemistry, and investigated empirical parameterisations of OH recycling and formation to yield the required changes in OH concentration. The Mainz Isoprene Mechanism (MIM2) used in the studies of Lelieveld et al. (2008) and Butler et al. (2008) was derived from MCM v3.1, the reference mechanism used in the present work; whereas Kubistin et al. (2008) used MCM v3.1 itself. The important point here is that our mechanism sensitivity impacts are directly relevant to the previous model-measurement comparisons using MIM2 through well-documented mechanism traceability. It is also noted that the relative performance of MCM v3.1, MIM2 and a series of other mechanisms (GEOS-CHEM, MOZART v4, CBM-05, STOCHEM and CRI v2) has also recently been compared by us (Archibald et al., 2009), using the same box model as applied in the present paper – so that the results of the present sensitivity tests can also be compared directly with inter-mechanism variability over a wide range of conditions. In addition, it should be noted that the paper does actually include numerous comparisons with, and discussions of, observational data. These first describe how the performance of the MCM v3.1 base mechanism provides a good description of data from laboratory and chamber systems (in section 2); and presentation of the output of several of the considered mechanistic variants with field observational data for carbonyl ratios, as summarised recently by Karl et al. (2009) (in section 3.4).

The second objection is that the presented work does not build significantly on a number of existing publications (all of which we cite). Again, we strongly disagree on this point. This work presents a number of tests which have not been considered in the previous studies, and is therefore able to draw numerous new conclusions. These tests and conclusions include:

(i) The impact of including propagating channels for the reactions of HO2 with all acyl and beta-oxo RO2 radicals has not previously been tested in a detailed isoprene mechanism. The branching ratios applied to these reactions are based on reported experimental measurements, as evaluated recently by the IUPAC panel (www.iupac-kinetic.ch.cam.ac.uk).

(ii) The mechanism proposed by Peeters et al. (2009) has not previously been tested in a mechanism which contains a fully explicit representation of competing peroxy radical reactions, or with the secondary chemistry of the major hydroperoxy-methyl-butenal products represented.

(iii) The mechanism proposed by Peeters et al. (2009) has not previously been tested in specific relation to its impact on HOx concentrations under ambient conditions, only in an apparently incomplete form in relation to its impact on carbonyl product ratios by Karl et al. (2009). The present work establishes that the rapid photolysis of the hydroperoxy-methyl-butenal products is crucial to achieve enhancements in OH which are of the magnitude observed in the field. This important aspect of the Peeters work has invariably been overlooked in the previous applications or discussions.

(iv) The implementation of a traceable reduced version of all the considered mechanistic changes in a global CTM has not been carried out before. This has allowed the impact of processes which are both specific and non-specific to isoprene to be assessed. The implementation of propagating channels of RO2 + HO2 reactions (particularly for the acetyl peroxy radical) is shown to have a comparable globally-integrated impact to the isoprene-specific impacts, which are more confined to high isoprene/low NOx regions.

Ref 1: comment 1:

The present study includes a scheme proposed by Peeters et al. (2009) and supports their findings of increased HOx production rates based on newly proposed isomerisation reactions. Reaction rates of these isomerization reactions have not yet been experimentally verified. An experimental study by Paulot et al. (2009) reports an upper limit for the Yield of (2Z)-hydroperoxymethylbutenol which is derived from the 1,6 shift reaction. Archibald et al. present this fact as a sufficient condition, yet their results show a 2-3 fold overestimation suggesting significant uncertainty in the 1,6 shift reaction rates or other mechanistic differences. No real explanation is given.

Response to comment 1:

It is not entirely clear what the referee's objection is here. As indicated above, we present the first full appraisal of the mechanism proposed by Peeters et al. (2009) in a mechanism which contains an explicit representation of competing peroxy radical reactions, and with secondary chemistry of the major hydroperoxy-methyl-butenal products represented. The results show that it is the only mechanistic change of those considered which yields changes in OH concentrations which approach those required to address the model-measurement discrepancies reported in the studies cited above. All the other considered sensitivity tests have very little effect on OH. In view of this potential, we conclude that it is important that the Peeters et al. (2009) mechanism is confirmed or refuted by appropriately-designed laboratory experiments.

As indicated by the referee, we discuss the results of Paulot et al. (2009), which provide observational evidence for the Peeters isomerisation mechanism through detection of the hydroperoxy-methyl-butenal product(s). We comment that the hydroperoxy-methyl-butenal yield reported by Paulot suggests that the competition of the RO2 isomerisation reactions with the RO2 +HO2 reactions may be about a factor of 2 to 3 lower than calculated by Peeters (although it is noted here that the hydroperoxy-methyl-butenal concentration may be heavily suppressed by rapid photolysis under the blacklight-photolysis conditions employed by Paulot). For this reason we present the results of a sensitivity test in which the RO2 isomerisation rates are reduced by an order of magnitude but still shown to have an effect under the simulated atmospheric conditions.

Not mentioned by the referee, we also make a point of referring to, and discussing the implications of, the kinetics studies of Perrin et al. (1998) and Jorand et at. (2003), which report clear experimental evidence for analogous isomerisations of delta-hydroxy peroxy radicals formed in alkane systems. These lend credence to the work of Peeters since the cis conformers of the delta-hydroxy isomers in the isoprene system have the key groups constrained in a favourable configuration and instinctively the isomerisations might be expected to be more important than in the alkane systems.

In our opinion, therefore, the referee's comment seriously misrepresents what we have presented. We believe we have followed a rigorous scientific procedure in testing and reporting the results; and have gone further in discussing the relevant literature than previous studies which have commented on the Peeters et al. (2009) mechanism.

Ref 1: comment 2:

A recent study by Karl et al. (2009) suggested significant changes in OVOC distributions as a result of some isomerization reactions proposed by Peeters et al. (2009). It is suggested that neglecting certain RO2 radical reactions and underestimation of HO2 reaction rates could have caused these OVOC shifts reported by Karl et al. (2009) (e.g. MVK/MAC). In order to reconcile the Peeters et al. (2009) mechanism with OVOC observations Karl et al. (2009) suggested relative changes in the isomerization reactions; qualitatively MVK/MAC ratios up to 6 at higher NOx (Archibald et al., Figure 6) seem to support conclusions drawn by Karl et al. (2009). It is not clear why Archibald et al. spend so much text on trying to rebut results by Karl et al. (2009), while at the same time not discussing the results in context of a vast body of literature on isoprene oxidation products! Just to give one example: to my knowledge MVK/MAC ratios up to 6 have never been observed in the real atmosphere (even at high NOx) and are typically much less than modeled by Archibald et al. (e.g. Stroud et al., Isoprene and its oxidation products, methacrolein and methylvinyl ketone, at an urban forested site during the 1999 Southern Oxidants Study, JGR, 2001; Spaulding et al., Characterization of secondary atmospheric photooxidation products: Evidence for biogenic and anthropogenic sources, JGR, 2003). Archibald et al. argue that tuning certain RO2 reaction channels instead of the isomerization reaction channels could bring OVOC distributions in line with observations at low NOx and suggest experimental verification; without presenting this experimental verification though it is not clear how much more insight can be inferred on this issue given that the MCM isoprene scheme seems to have other significant uncertainties.

Response to comment 2:

We would like to start by emphasising that we think the study of Karl et al. (2009) is an interesting, important and very valuable piece of work which contains a large amount of information over and above its discussion of the mechanism proposed by Peeters et al. (2009). It is, nonetheless, quite negative about the Peeters mechanism, based on its apparent unfavourable impact on simulated carbonyl product ratios and suppression of hydroxyacetone formation. In view of the unique potential of the Peeters mechanism for substantial OH recycling found in our work, it was imperative that we entered into some discussion of the Karl et al. (2009) appraisal.

Implementation of the Peeters mechanism in our box model led to some similar effects to those reported by Karl, but also to some important differences. Based on the information presented by Karl et al. (particularly in their Table A3), we interpret the differences as being due (at least in part) to differences in the representations of competing RO2 radical reactions, and an apparent lack of a representation of the further chemistry of the hydroperoxy-methyl-butenal isomers (particularly their rapid photolysis). We find that the former has an influence on carbonyl product ratios (such as MVK/MAC), whereas inclusion of the latter could be a relatively prompt source of hydroxyacetone and other secondary products. We therefore could not avoid the conclusion that the implementation of the Peeters mechanism in the work reported by Karl et al. (2009) was apparently truncated and incomplete, and that this might contribute to its unfavourable performance. We acknowledge, however, that we did not comment on the parameter sensitivity test performed by Karl et al. (mentioned by the referee), and a suitable discussion of this will be included in a revised manuscript. The Peeters mechanism is, of course, a reaction framework with scope for some variation of parameter values within that framework.

The referee comments that MVK/MAC ratios of almost 6 that we simulate at the high end of the considered NOx range with the Peeters mechanism variants (Mechanisms 3a and 3b) have not been observed in the field. As shown in Figure 6, these ratios are simulated at average NOx mixing ratios of about 8-11 ppb, with the ratios falling with decreasing NOx (e.g. to about 2 at 1 ppb NOx). Although not shown in the paper, the ratio also falls with increasing NOx as the onward reactions of the isoprene RO2 radicals with NO become progressively more dominant over back-decomposition – thereby inhibiting the redistribution of the peroxy radical population. Indeed, in the high NOx limit, the mechanism predicts yields of MVK, MACR and HCHO which are consistent with those reported in laboratory studies at ppm and greater levels of NOx. Consequently, the maximum ratio of nearly 6 can only be achieved with oxidation of isoprene at a controlled level of NOx of about 10 ppb. An observation under polluted atmospheric conditions always represents an average over a range of conditions, so that would be essentially impossible for MVK/MAC ratios approaching this maximum to be observed in the field, with the Peeters mechanism operating. Inspection of the studies of Stroud et al. (2001) and Spaulding et al. (2003), mentioned by the referee, indeed show a wide variability in NOx levels. It should also be noted that some combustion sources emit methacrolein directly, which potentially has an isoprene-independent reducing effect on MVK/MAC in polluted environments.

The referee comments that we argue for "tuning certain RO2 reaction channels" to address the issue of carbonyl ratios. In practice, we actually argue for using a mech-

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anism which uses an adequate representation of potentially competing RO2 reactions with rate coefficients based on reported kinetics studies. No "tuning" is involved. The study of Karl et al. (2009) uses incorrect rate coefficients and probably a less than adequate representation of the reactions of RO2 with the peroxy radical pool. We understand that these are based on the representation in Mozart v4, which we have previously found lead to a divergence in performance (in specific respect to simulations of HO2 and RO2) at low NOx compared with a suite of mechanisms (Archibald et al., 2009). As a result, the MVK/MAC vs NOx plot reported in the discussion comment of Karl (ACPD 9, C3775–C3783, 2009) as attributed to the Peeters mechanism (with MVK/MAC ratios up to over 12), differs markedly from that in Figure 6 of our paper.

The referee finally comments that "the MCM isoprene scheme seems to have other significant uncertainties" and that the work with it generally has a lack of experimental verification and insight. Whilst we acknowledge that the isoprene chemistry in the MCM (and all other current mechanisms) cannot explain all observations, it is nonetheless firmly based on laboratory kinetics and mechanistic studies (as described in section 2). It provides a good representation of laboratory product yields at high and zero NOx (as described in section 2) and has been evaluated against chamber data (Saunders et al., 2003; Pinho et al., 2005). The MCM is therefore at least as experimentally-verified as any other mechanism available, and probably more so. It provides an ideal base mechanism for a detailed mechanism sensitivity test such as that presented here, and we strongly disagree that our methodology cannot deliver new insights.

Ref 1: comment 3:

The overall (MVK+MAC)/isoprene ratio becomes systematically low under clean (low NOx) conditions. (see Figure 6). Measurements by Helmig et al. (JGR, 1998) show that this ratio can reach 2-3 in certain regions of the PBL in the remote tropical atmosphere (no biomass burning / low NOx). Kuhn et al. (ACP, 2007) present (MVK+MAC)/isoprene ratios on the order of 2-10 between 1000 and 2000 m above ground (ACP, 2007). It appears that the upper PBL limit in the present modeling study can at most reach

0.5 under these conditions, even at relatively high NOx (e.g. 1 ppbv NOx, figure 6, Archibald et al.). This could be 6-50 times lower compared to observations.

Response to comment 3:

Because isoprene is the emitted compound and MVK and MAC are relatively unreactive products, the (MVK+MAC)/isoprene ratio can of course show enormous variability; with elevated values away from the source (both laterally and vertically) when the reactive isoprene is almost completely depleted but the less reactive MVK and MAC remain at significant levels. Elevated ratios will also potentially occur at night-time in the forested boundary layer when the isoprene source is switched off but MVK and MAC remain. The presented calculations specifically illustrate daytime conditions close to source.

Ref 1: comment 4:

Archibald et al. put their modeling efforts in context of the GABRIEL campaign. Observed HO2/HO ratios of 234 were reported (see. Kubistin et al., ACPD, 2008). From figure 3 I estimate model ratios on the order of 1800 at low NOx. No discussion is given on why the modified MCM model predicts such different partitioning at low NOx.

Response to comment 4:

The referee raises a valid point, which highlights a widely reported discrepancy between modelled and observed HO2/OH ratios. A number of studies have shown that all mechanisms tend to overestimate the ratio at low NOx, compared with observations (e.g., Chen et al., 2009 and references therein). It should be emphasised, therefore, that this discrepancy is neither specific to isoprene-dominated environments nor to investigations using the MCM chemistry. It potentially has contributions from both measurement issues and chemical mechanism issues. With regard to the former, it should be noted that comparison of a temporally or spatially-averaged measurement with an idealised simulation can be misleading if there are small-scale fluctuations in NOx.

This is because HO2/OH measurements over a range of NOx levels at low NOx will be lower than the HO2/OH ratio at the average level. This is because the HO2 level varies only mildly with NOx, whereas that of OH varies strongly and non-linearly with NOx. It is also noted that the model-measurement comparison can be influenced by imprecision in the measurements of the NOx species (particularly NO), if measurements are at very low NOx, close to instrumental detection limits. Chemical mechanism issues can relate to errors in the gas phase pathways, or to the lack of representation of a loss process (e.g., aerosol uptake) for HO2 – which potentially becomes more important at low NOx when the lifetime of HO2 with respect to gas phase loss increases.

The previous studies using the MCM or the traceable MIM2 (cited above) have reported model overestimations of HO2/OH. The referee quotes the observed HO2/OH ratio of 234 reported in the study of Kubisitin et al. (2008). The present simulation with MCM v3.1 for about the same NO level of 13 ppt as reported by Kubisitin et al. overestimates this ratio by about a factor of 4, which is similar to the value of 3.2 quoted by Kubisitin et al. (2008). Implementation of the full Peeters mechanism (Mechanism 3b) leaves this approximately unchanged, because the increased HO2 formation in conjunction with hydroperoxy-methyl-butenal formation is offset by OH formation from the efficient photolysis of the hydroperoxy-methyl-butenal. In view of the referee's comment some presentation and discussion of this issue will be given in a revised manuscript.

Ref 1: concluding comment:

In summary it appears that additions proposed by Archibald et al. still lead to significant discrepancies between observations and models. For the reasons mentioned above it can not be claimed that these additions resolve the majority of issues with the MCM isoprene scheme and that the presented model results can be reconciled with observations. Without new observational data it is not possible to judge on the accuracy of certain modifications proposed by Archibald et al. (e.g. modifications according to Peeters et al., 2009).

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Response to concluding comment:

We reiterate that our study is an isoprene mechanism sensitivity investigation, which systematically appraises a number of mechanistic changes which are based on recently reported experimental and theoretical studies. Contrary to the referee's assertion, we do not claim to have resolved the majority of issues related to isoprene chemistry, and we do not unconditionally recommend the mechanism proposed by Peeters et al. (2009). What we have done is to apply a well-established and appropriate method to analyse and report the sensitivity of the isoprene system to the series of mechanistic changes over a wide range of atmospherically-relevant conditions; and to provide a detailed discussion of the results. We believe we have followed a rigorous scientific procedure in testing and reporting the results, and that the work can help to inform ongoing studies in this field.

References

Archibald, A. T., Jenkin, M. E., and Shallcross, D. E.: An isoprene mechanism intercomparison, Atmos. Environ., doi:10.1016/j.atmosenv. 2009.09.016, 2009.

Butler, T. M., Taraborrelli, D., Brühl, C., Fischer, H., Harder, H., Martinez, M., Williams, J., Lawrence, M. G. and Lelieveld, J.: Improved simulation of isoprene oxidation chemistry with the ECHAM 5/MESSy chemistry-climate model: lessons from the GABRIEL airborne field campaign, Atmos. Chem. Phys., 8(16), 4529-4546, 2008.

Chen, S., et al., A comparison of chemical mechanisms based on TRAMP-2006 field data, Atmos. Environ., doi:10.1016/j.atmosenv.2009.05.027, 2009.

Emmerson, K. M. and Evans, M. J.: Comparison of tropospheric gas-phase chemistry schemes for use within global models, Atmos. Chem. Phys., 9, 1831–1845, 2009.

Jorand, F., Heiss, A., Perrin, O., Sahetchian, K., Kerhoas, L. and Einhorn, J.: Isomeric hexyl-ketohydroperoxides formed by reactions of hexoxy and hexylperoxy radicals in oxygen, Int. J. Chem. Kinet., 35(8), 354-366, 2003.

Karl, T., Guenther, A., Turnipseed, A., Tyndall, G., Artaxo, P. and Martin, S.: Rapid formation of isoprene photo-oxidation products observed in Amazonia, Atmos. Chem. Phys., 9, 7753–7767, 2009.

Kubistin, D., Harder, H., Martinez, M., Rudolf, M., Sander, R., Bozem, H., Eerdekens, G., Fischer, H., Gurk, C., Klüpfel, T., Königstedt, R., Parchatka, U., Schiller, C. L., Stickler, A., Taraborrelli, D., Williams, J. and Lelieveld, J.: Hydroxyl radicals in the tropical troposphere over the Suriname rainforest: comparison of measurements with the box model MECCA, Atmos. Chem. Phys. Discuss., 8(4), 15239-15289, 2008.

Kuhn M. et al.: Intercomparison of the gas-phase chemistry in several chemistry and transport models, Atmos. Environ., 32, 693-709, 1998.

Lelieveld, J., Butler, T. M., Crowley, J. N., Dillon, T. J., Fischer, H., Ganzeveld, L., Harder, H., Lawrence, M. G., Martinez, M., Taraborrelli, D. and Williams, J.: Atmospheric oxidation capacity sustained by a tropical forest, Nature, 452(7188), 737-740, 2008.

Paulot, F., Crounse, J. D., Kjaergaard, H. G., Kürten, A., St. Clair, J. M., Seinfeld, J. H. and Wennberg, P. O.: Unexpected epoxide formation in the gas-phase photooxidation of isoprene. Science, 325, 730-733, 2009.

Peeters, J., Nguyen, T. L. and Vereecken, L.: HOx radical regeneration in the oxidation of isoprene, Phys. Chem. Chem. Phys., 28, 5935-5939, 2009.

Perrin, O., Heiss, A., Doumenc, F. and Sahetchian, K.: Determination of the isomerization rate constant HOCH2CH2CH2CH(OO.)CH3 → HOC.HCH2CH2CH(OOH)CH3. Importance of intramolecular hydroperoxy isomerization in tropospheric chemistry. J. Chem. Soc. Faraday Trans., 94, 2323–2335, 1998.

Pinho, P. G., Pio, C. A. and Jenkin, M. E.: Evaluation of isoprene degradation in the detailed tropospheric chemical mechanism, MCM v3, using environmental chamber data. Atmos. Environ., 39, 1303-1322, 2005.

Poechl, U., Von Kuhlmann, R., Poisson, N. and Crutzen, P. J.: Development and intercomparison of condensed isoprene oxidation mechanisms for global atmospheric modelling, J. Atmos. Chem., 37, 29–52, 2000.

Saunders, S. M., Jenkin, M. E., Derwent, R. G. and Pilling, M. J.: Protocol for the development of the Master Chemical Mechanism, MCM v3 (Part A): tropospheric degradation of non-aromatic volatile organic compounds, Atmos. Chem. Phys., 3, 161-180, 2003.

Spaulding, R. S., Schade, G. W., Goldstein, A. H. and Charles, M. J.: Characterization of secondary atmospheric photooxidation products: Evidence for biogenic and anthropogenic sources, J. Geophys. Res., 108(D8), 4247, doi:10.1029/2002JD002478, 2003.

Stroud, C. A. et al.: Isoprene and its oxidation products, methacrolein and methylvinyl ketone, at an urban forested site during the 1999 Southern Oxidants Study, J. Geophys. Res., 106(D8), 8035-8046, 2001.

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 5863, 2010.