**Atmospheric
Chemistry
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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.

Anonymous Referee #1

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

Apart from this general comment I have a number of specific comments:

(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 isomerization 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.

(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.

(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.

(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.

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).

References: Archibald et al., Atmos. Environ., 2009. Butler et al., ACP, 2007. Helmig et al., JGR, 1998. Karl et al., ACP, 2009. Kubistin et al., ACPD, 2008. Kuhn et al., ACP, 2007. Lelieveld et al., Nature, 2008. Paulot et al., Science, 2009. Peeters et al., PCCP, 2009. Pugh et al., ACPD, 2010. Silva et al., ES&T, 2010. Spaulding et al., JGR, 2003. Stroud et al., JGR, 2001.

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