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.

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We are very grateful to Dr Karl for considering some of the parameter adjustments we highlighted in our discussion of isoprene-derived peroxy radical chemistry, and for posting the results as a discussion comment. Dr Karl has implemented a differential reactivity with respect to the reactions of the peroxy radical pool with the tertiary peroxy radical 1-OH-2-OO (or ISOPBO2 in our notation) and with the secondary peroxy radical 4-OH-3-OO (or ISOPDO2 in our notation); and has increased the rate coefficient for the reactions of HO2 with all the isoprene-derived peroxy radicals to a value based on experimental study. This has nudged the simulated methylvinyl ketone/methacrolein (MVK/MAC) ratio to a slightly lower value.

It appears that the respective formation of MVK and MAC from the reactions 1-OH-

2-OO and 4-OH-3-OO with the peroxy radical pool is not represented (based on the information given in Figure 2 of the comment), and this may nudge the MVK/MAC ratio slightly lower again, because the latter reaction (forming MAC) is more efficient than the former (forming MVK). The formation of MVK and MAC from these reactions explains why these products are observed in NOx-free laboratory experiments, and the differential reactivity of 1-OH-2-OO and 4-OH-3-OO explains why the observed MVK/MAC yield ratio switches from >1 in the presence of high NOx, to <1 in the absence of NOx (e.g., Ruppert and Becker, 2000; Lee et al., 2005).

Having reconsidered the results of our simulations for the specific NO levels of the AMAZE campaign, we acknowledge that we do simulate MVK/MAC ratios that are greater than those measured (as reported by Karl et al., 2009) using the Peeters mechanism variants, and that our discussion did not reflect this adequately. At 100 ppt NO, the Mechanism 3a and 3b variants lead to respective MVK/MAC ratios of about 2 and 2.5, which are therefore significantly greater than the reported value of (1.38 +/- 0.10). These are still lower than reported by Dr Karl, such that remaining differences are due to the cumulative impacts of a number of other mechanistic features (e.g., a small contribution of isoprene ozonolysis; and partial formation of hydroxymethylvinyl ketone from ISOPBO in our simulations) and differences in modelling method. In the revised version of the manuscript, we have therefore adjusted our discussion accordingly to reflect the above; and have included comment on the parameter sensitivity test reported by Karl et al. (2009) to indicate that the Peeters mechanism is a reaction framework with scope for variations of parameter values within that framework (which, of course, ultimately requires experimental validation). We do note, however, that the reported range of MVK/MAC and (MVK+MAC)/isoprene can be recreated in our simulations, if isoprene oxidation occurs at a lower NO level of about 30-60 ppt.

Finally, we clarify here a point raised by Dr Karl. He is correct that the MCM does not represent all peroxy radical permutation reactions explicitly. Representing such reactions for the 1000 peroxy radicals in the full MCM would require about 0.5 million

reactions, each with up to three product channels. Even representing such reactions for the 38 peroxy radicals in the full isoprene scheme in the present study (Mechanism 4) would require over 700 reactions, again each with up to three product channels. The mechanism therefore uses a parameterisation in which each peroxy radical reacts with the peroxy radical pool in a pseudo-unimolecular reaction, which allows a differential reactivity to be represented of the basis of the identity of each radical. This method is fully documented in Jenkin et al. (1997) and Saunders et al. (2003), and indeed the impact of implementing the parameterisation was specifically tested for first generation OH-initiated isoprene chemistry by Jenkin et al. (1997). This allowed it to be tested against chamber results and confirmed that it was able to recreate the switch in MVK/MAC yield ratio on going from NOx present to NOx absent conditions, as commented on above. The parameters were subsequently updated, as described by Saunders et al. (2003), to reflect new kinetic data reported for structurally similar peroxy radicals (Jenkin et al., 1998).

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