

Reviewer report revised manuscript for ACP “The MCM v3.3.1 degradation scheme for isoprene”, by Jenkin et al.

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General comment

In both the author response and in the revised version of this manuscript, all comments and remarks of the two reviewers and of a commentator have been addressed, most of them adequately, yet some points deserve a few more lines clarification, as detailed below. Therefore, the revised version of this work, which will be of great value to atmospheric modelers, is recommended for publication in Atmospheric Chemistry and Physics, after minor additional revision.

Specific comments

1. Re: Peroxy radical reactions, p.6, lines 18-21 and p.12, lines 1-4

In the approach of this work, the scaling procedure used for the 1,6 H shift rate is the proper way to reproduce the experimental bulk peroxy isomerization rate leading to HPALDs of Crouse et al., 2011. However, this $k(\text{bulk})$ is determined by the product of the specific rate coefficients $k(1,6\text{-H})$ of the isomerizing $Z\text{-}\delta\text{-OH-peroxys}$ and their steady-state population fractions $f(Z\text{-}\delta)$, the latter depending on a large number of uncertain kinetic parameters, in particular the $k(1,6\text{-H})$ themselves (since the fast 1,6-H shift keeps the $[Z\text{-}4\text{-OH-1-O}_2]/[4\text{-OH-3-O}_2]$ ratio well below equilibrium) and the k of the various O_2 -addition and O_2 -loss reactions. It follows that the scaling factors found this way will reflect the uncertainties on all these parameters. In the updated “LIM1b” mechanism (Peeters 2015), the O_2 -addition branching fractions toward the $E\text{-}\delta\text{-OH-isoprenyl peroxys}$ were increased by a factor of 2, at the expense of the $Z\text{-}\delta\text{-OH-isoprenyl peroxys}$, in order to satisfy the twice higher than LIM1-predicted $E\text{-}\delta\text{-OH-isoprenyl nitrates}$ observed by Crouse et al. (2014). This leads to scaled $k(1,6\text{-H})$ values in LIM1b that are about 1.5 times higher than found in this work. Moreover, for fixed values of all parameters above except the $k(1,6\text{-H})$ themselves, according to box modeling by J.-F. Müller, the derived $k(1,6\text{-H})$ will show a power dependence on the *total* bulk isomerisation rate of $\sim k_t(\text{bulk})^{1.7}$ at 295 K and $k_{tr} = 0.02 \text{ s}^{-1}$ (through the strong “feedback” effect of $k(1,6\text{-H})$ for the $Z\text{-}4\text{-OH-1-O}_2$ peroxys). This means that the stated uncertainty of $\pm 50\%$ on the $k(\text{bulk})$ of 0.002 s^{-1} of Crouse et al. (2011) results in an uncertainty of $+100\%/-70\%$ for the scaled $k(1,6\text{-H})$. The uncertainty on the branching ratio di-HPCARPs:HPALDs will even widen that uncertainty range on the scaled $k(1,6\text{-H})$. A few lines should therefore be inserted on p.6 or p.11 pointing out the strong dependence of the derived $k(1,6\text{-H})$ on several of the adopted but not well-known kinetic parameters, such as those of the O_2 -addition and O_2 -loss reactions, and the *total* bulk isomerization rate itself.

2. Re: Oxy radical reactions, p.7 lines 26-31 and p.8 lines 1-9.

The comment on the first manuscript version regarding the very fast $E\text{-to-Z}$ conversions of the enoxy radicals ISOPAO and ISOPCO as predicted by Nguyen and Peeters (2015) is

addressed in the last lines of this paragraph, but only fleetingly. The reader deserves to be informed that in particular for ISOPCO the newly-characterized conversion to CISOPCO is predicted to be *4 orders of magnitude* faster than its reaction with O₂ (even an unlikely error of 2 kcal/mol on the high-level computed barrier would still leave the *E*-to-*Z* conversion far faster), such that the mechanism retained for ISOPCO (Fig. 2) is likely incorrect, though the effects on the products remain relatively minor (HC₄CCHO would be replaced largely by its isomer HC₄ACHO and by some GLYOX + ACETOL).

3. Explanatory note: comment on 1st version. Improving the MVK/MACR ratio and the absolute MVK and MACR yields.

The author response stated that the first technical comment on the original ms version was unclear. It was indeed too concise: “p. 9716, line 28: Though this path is of minor interest, it might be stated that this route for ISOP34O₂ was proposed and argued by Peeters et al., 2014 (in the SI)”. It referred to a sentence, last line p. 5 and first lines p. 6 of the mentioned SI, on the fate of specifically the 3-OH adducts, to the effect that if Park et al. (2003) had used their highest-level CCSD(T) energy data in their RRKM/ME analysis instead of the lower-level B3LYP energies, they would have found that the initial, hot 3-OH-4-O₂ peroxy isomer (IIIa in Park) is collisionally stabilized as such for close to 90% (instead of undergoing cyclic isomerization for a reported 47%), *such that in fact almost all 3-OH reacts through ISOP34O₂ as shown in Fig. 2.*

This would result in about 2% more MACR than in the present version of this work, and hence a modeled MVK/MACR ratio closer to the often observed ~1.5. That the absolute MVK and MACR yields are then both somewhat too high, is remedied by having a larger fraction of the 1-OH- and 4-OH adducts react with O₂ to form *E*- δ -OH-isoprenyl peroxy, in accordance with the conclusions of Crouse et al. (2014) (see comment 1). At high NO, the latter peroxy, via the very fast *E*-to-*Z* enoxy conversions (Nguyen and Peeters, 2015; see comment 2), would then result mainly in more C₅-hydroxycarbonyls from both major OH-adducts.

Typos

p. 16 line 31: “..., because they allow a...” (delete “are”)

p. 17, line 21: “.... on information provided...” (“on” is missing)

p. 17, line 25: “...C₅ oxy radical in each case (see Fig. 9)” (9 instead of 8)

p. 23, line 10: “...from the significant operation of the newly implemented...” (“of” is missing)

References: as in the revised manuscript