

Jozef Peeters

Department of Chemistry, University of Leuven, Belgium

General comment

An upgrade of the MCM mechanism for isoprene oxidation as in this manuscript was indeed necessary in order to implement the new peroxy radical interconversion and isomerization chemistry and subsequent OH regeneration of the Leuven Isoprene Mechanism (Peeters et al., 2009 and 2014, Peeters and Muller, 2010), as well as the new chemistry of MACR oxidation (Crouse et al., 2012; and Kjaergaard et al., 2012) and some other recent new insights in the oxidation of this major atmospheric VOC. Much work towards that objective was performed and is reported in this extensive manuscript, implementing a large number of additional reactions involving a great many new intermediates. However, as detailed below, some of the (unnecessary) simplifications in this work result in MCM model predictions that are sharply at odds with both theoretical and experimental (new) findings, concerning the distribution of major products under near-pristine conditions of low NO as in remote tropical forests. Also, some recently reported new insights in relevant enoxy radical chemistry, with bearing on products at high NO, appear to have escaped the attention of the authors. Since the oxidation of isoprene, with its great impact on tropospheric chemistry, deserves and needs model-representations as close as possible to present knowledge, some major revisions of the presently reported mechanism are in order.

Specific comments

1. The rate coefficients for O₂ addition to the initial hydroxyl-isoprenyl adducts and for redissociation of the various resulting peroxys, denoted here as $k(+O_2)$ and $k(-O_2)$, were adapted from the upgraded Leuven Isoprene Mechanism LIM1 (which should be referred to as such) of Peeters et al. (2014). However, it is not clear why averages are taken for “similar” structures; there are no rational grounds for it, nor does it simplify the model, but leads to unintended, fairly serious problems as detailed below. A first problem arises because the averaging is inconsistent: for the $k(-O_2)$ of the *Z*- δ -OH-isoprenyl peroxys, the average is taken of the LIM1 k -values for the 1-OH-4-OO and 4-OH-1-OO peroxys (using the notations of Peeters et al., 2009 and in the footnotes of Table S1 of this work), and likewise for the $k(-O_2)$ of the *E*- δ -OH-isoprenyl peroxys; for the $k(-O_2)$ of the β -OH-isoprenyl peroxys on the other hand, the averaging is done in a different way: separately for 1-OH-2-OO and 4-OH-3-OO, each time taking the average of the LIM1 $k(-O_2)$ to yield the *cis*- and *trans*-OH adducts. The $k(-O_2)$ for 1-OH-2-OO and 4-OH-3-OO should indeed be different (on account of the

difference in stability of the resulting 1-OH and 4-OH hydroxyl-adducts), but the same applies for the two *Z*- δ -OH peroxys. The unintended result of this inconsistent averaging in MCM 3.3 is that the equilibrium constants for the highly important (indirect) β -OH-isoprenyl peroxy \leftrightarrow *Z*- δ -OH-isoprenyl peroxy interconversions become very different for the two peroxy subpools from the 1-OH and 4-OH adducts. Thus, according to this **MCM** update: $\text{Keq1}(1\text{-OH-2-OO} \leftrightarrow \text{Z-1-OH-4-OO}) = 1.8 \times \exp(-980/T)$, or **Keq1(295) = 0.065**; and $\text{Keq2}(4\text{-OH-3-OO} \leftrightarrow \text{Z-4-OH-1-OO}) = 2.22 \times \exp(-1590/T)$, or **Keq2(295) = 0.010**, i.e. differing by a factor of 6.5. However, the high-level-computed **LIM1** equilibrium constants are nearly identical ($\text{Keq1} = 1.93 \times \exp(-1484/T)$ or **Keq1(295) = 0.013**; and $\text{Keq2} = 1.96 \times \exp(-1451/T)$ or **Keq2(295) = 0.014**, respectively) as they should: in both cases the difference in stability is mainly due to the H-bond in the 8-member cyclic *Z*- δ -OH-peroxys being about 2 kcal/mol weaker than in the 6-member cyclic β -OH-peroxy counterparts. Note that the experimentally derived Keq for 1-OH-2-OO \leftrightarrow *Z*-1-OH-4-OO and 1-OH-2-OO \leftrightarrow *E*-1-OH-4-OO reported by Crouse et al. at the ACM conference, Dec. 2014, agree with LIM1 within $\pm 30\%$. Since the steady-state populations $f(\text{Z-}\delta)$ of the isomerizing *Z*- δ -OH-peroxys — which together with the $k(1,6\text{-H})$ rate coefficients determine the bulk peroxy isomerization rates — will tend to the mentioned Keq at low “traditional” peroxy removal rates k_{tr} (see LIM1 paper), the much too high Keq1 for the 1-OH-peroxys will have a drastic impact on the relative and absolute importance of the isomerization yields of the two peroxy pools at low k_{tr} . (Put in a different way: the $k(-\text{O}_2)$ of *Z*-1-OH-4-OO in MCM being relatively too low compared to that of 1-OH-2-OO results in a much too high steady-state population fraction $f(\text{Z-}\delta)$ for the 1-OH-peroxys at low k_{tr} .) The consequences of this will be discussed below.

2. The isomerization rate coefficient $k(1,6\text{-H})$ is assumed equal in the manuscript for the two peroxys *Z*-1-OH-4-OO and *Z*-4-OH-1-OO, and is derived from the experimental $k(\text{bulk})$ of Crouse et al. (2011) at $k_{\text{tr}} = 0.021 \text{ s}^{-1}$, giving $k(1,6\text{-H}) \approx 0.10 \text{ s}^{-1}$ at 295 K. The reason for the low value is simply the much too high population fraction $f(\text{Z-}\delta)$ of *Z*-1-OH-4-OO at this k_{tr} , as discussed above. Also, as shown by modelling performed by J.-F. Müller, it follows that the majority of the isomerization would then be due to the peroxy pool from 1-OH, for example 77% at $k_{\text{tr}} = 0.1 \text{ s}^{-1}$, implying a **HPALD1/HPALD2 yield ratio of 3.3**. This is very far from the measured HPALD1/HPALD2 yield ratio of only ~ 0.2 of Crouse et al. (ACM, 2014). This major discrepancy is also caused by the assumption in the present MCM that both $k(1,6\text{-H})$ would be equal; the LIM1 computations, at all levels of theory (B3LYP; M06-2X; CCSD(T)), show a barrier height for the 1,6-H shift in *Z*-4-OH-1-OO about 1.5 kcal/mol lower than in *Z*-1-OH-4-OO, meaning that the former should isomerize about 10 times faster, confirming and rationalizing the measured HPALD1/HPALD2 yield ratio of Crouse (2014). The high theoretical $k(1,6\text{-H } Z\text{-4-OH-1-OO})/k(1,6\text{-H } Z\text{-1-OH-4-OO})$ ratio of ≈ 10 (Peeters et al., 2009; and LIM1, 2014) is also required to explain another recently reported finding of Crouse et al. (ACM, 2014): at low k_{tr} of $\sim 0.01 \text{ s}^{-1}$, the measured ratio of products from 1-OH-2-OO and 4-OH-3-OO (such as MVK/MACR) **increases to ~ 4** , much higher than the ratio around 1.5 – 2 at higher k_{tr} . This is because a major part of the 4-OH peroxy pool effectively isomerizes at low k_{tr} , leaving little room for MACR production. (In fact, from this result one can derive that the total isomerisation yield at 295 K and k_{tr} of 0.01 s^{-1} is around

20 – 24%, a factor ~1.5 lower than the LIM1 prediction). However, the present MCM (Section 3.2.5 and Fig. 15) predicts a quite different evolution of the MVK/MACR ratio: a **decrease** for lower ktr to even below **1.0**, due to the implied much too high $f(Z-\delta)$ for the 1-OH peroxy pool (see above), and hence less production of MVK at low ktr. This major discrepancy of the present MCM version from both theory and experiment should be addressed and remedied. The more so, as modelling (by J.-F. Müller) shows that the bulk isomerization rate and yield in the present MCM are nearly 3 times too low compared to experiment at high ktr of ~4 s⁻¹ (Crouse et al. 2011, experiment at 295 K and 19 ppb NO).

3. However, the above does not suggest to merely adopt the LIM1 kinetic parameters in MCM. Another, major conclusion from the recently reported experimental result of Crouse et al. (ACM, 2014) is that the β -OH-peroxy \leftrightarrow Z- δ -OH-peroxy (quasi-)equilibration occurs about 5 times faster than in LIM1. Note that in the LIM1 work, only the equilibrium constants Keq for the various O₂-addition and O₂-loss reactions (and hence also for the indirect peroxy interconversions) were calculated, **not** the rate coefficients for these forward or reverse reactions. The various individual k(+O₂) were derived in LIM1 as the product of the (highly uncertain) overall O₂-addition rate constant from the literature and the branching fractions estimated from the known product distribution at high NO, and the k(-O₂) were then found from k(+O₂)/Keq. Given that the Keq of LIM1 for the interconversions are confirmed within $\pm 30\%$ by experiment (Crouse et al., ACM, 2014, see above), the most straightforward explanation for the faster equilibration than in LIM1 is that the overall O₂-addition rate to the OH-adducts is 5 \times higher than the literature value adopted in LIM1, i.e. should be 5 \times 10⁻¹² (as recommended by Atkinson.), entailing 5 times higher values for all individual k(+O₂) and k(-O₂) of LIM1, all calculated Keq remaining unchanged. This speeds up the interconversions, bringing them in line with the recent findings of Crouse et al. (ACM, 2014), and substantially increases the predicted isomerisation yield of the 4-OH peroxy pool for ktr below 0.1 s⁻¹. However, the overall isomerisation yield at lower ktr (0.01 – 0.1 s⁻¹) becomes somewhat too high, and the departure from the Crouse et al. results (both 2011 and ACM, 2014) at high ktr is not sufficiently reduced. A good fit with the Crouse et al. data of 2011 and with the recent other data reported by Crouse (ACM, 2014), including the MVK/MACR and HPALD1/HPALD2 ratios and their behavior as function of ktr, is achieved — in addition to the 5-fold increase of all k(+O₂) and k(-O₂) — by reducing both the k(1,6-H) of LIM1 by a factor of 3, to become in the optimized **LIM1b** mechanism: $k(1,6\text{-H } Z\text{-1-OH-4-OO}) = 1.3 \times 10^{10} \times \exp(-8591/T) \times \exp[10^8/T^3]$ s⁻¹ or 0.14 s⁻¹ at 295 K; and $k(1,6\text{-H } Z\text{-4-OH-1-OO}) = 3.6 \times 10^{10} \times \exp(-8174/T) \times \exp[(10^8)/T^3]$ s⁻¹ or **1.6** s⁻¹ at 295 K. The latter in particular is still much higher than the **MCM value of 0.10** s⁻¹! (Note that an overestimation of the theoretical k(1,6-H) in LIM1 might be ascribed to a too high tunneling factor estimated in the asymmetric Eckart barrier approximation.)
4. Concerning the reactions of the radicals ISOPCO and ISOPAO (section 2.1.3 and Fig. 2), it was shown in a recent article of Nguyen and Peeters (web-published Feb. 6, 2015) that these substituted allyloxy or enoxy radicals, *E*-4-OH-1-O and *E*-1-OH-4-O, undergo very fast isomerizations to their Z-counterparts by a newly proposed mechanism, with rates, quantified

at high levels of theory (CCSD(T)), of $10^{(9)}$ s⁻¹, outrunning the respective reactions with O₂ and the 1,5-H shift isomerization of MCM (both proposed by Dibble, 2002), by some 5 and nearly 2 orders of magnitude, respectively. The paper therefore concluded that these *Entgegen* enoxy radicals *E*-4-OH-1-O and *E*-1-OH-4-O lead to exactly the same products as their *Zusammen* twins *Z*-4-OH-1-O (or CISOPCO, Fig. 2) and *Z*-1-OH-4-O (or CISOPAO), being for the larger part C5-hydroxycarbonyls (and HO₂), consistent with very recent results of Crouse et al. Revising the present MCM in this way will at the same time remedy the too low predicted C5-hydroxycarbonyl yield at high NO of only 11%, Table S2, compared to the measured yields of ~19% and 15% reported in the two studies that focused on such products (Zhao et al., 2004; and Baker et al., 2005). Also, that a sizable fraction (22%) of the radicals resulting from the 1,5-H shifts in CISOPAO and CISOPCO, would undergo concerted H₂O elimination and ring closure to form 3-methyl-furan, Figs. S1 and S2, is quite uncertain. The H₂O elimination and ring-closure step was only proposed but not theoretically characterized in the cited paper; even though the reactant is chemically activated, this complex four-center reaction, with TS featuring a 4-ring fused to a 5-ring, might face a too high energy barrier to compete with the O₂-addition rate of $\sim 10^{(7)}$ s⁻¹. Note also that Sprengnether et al. (2002) could not observe M3F as oxidation product at high NO in near wall-free conditions, supporting the view that M3F results from heterogeneous processes as argued by Dibble (2007). Omitting this reaction channel would bring the C5-hydroxycarbonyl yield in closer agreement with the experimental (gas phase) values .

5. Re the first-generation chemistry (section 2.1.4), it deserves mentioning on p. 9720, lines 10-12, that Peeters and Nguyen (2012) discussed the 1,4-H shift in the α -formyl peroxy radicals C526O₂ and C527O₂, for which they computed a barrier height of 20.2 kcal/mol and provided a rate estimate of 0.01 – 0.1 s⁻¹, and “stressed that this competing process [with the NO reaction] could therefore become important at the low or moderate NO levels of the PBL in less polluted regions”.

Technical comments and typos

- 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).
- p 9720, line 8: The term “postulated” is inappropriate (according to Webster, “postulate” means “to assume without the need to prove”); more correct would be here: “...the mechanism theoretically characterized by...”.
- p 9721, lines 2-3: The notations DHPMVK and DHPMACR do not seem appropriate, since these dihydroperoxycarbonyls do not feature an MVK or MACR base-frame, and are not derived from them. Further, for the complete chemistry discussed lines 9-13, the LIM1 paper (2014) should be cited, and specifically for the additional routes to methyl glyoxal and glyoxal, the “Addition and Correction” amendment of Crouse et al. (2012, see reference below).

- typo p 9733, line 25: "...in the ~~the~~ HO2 radical..."
- typo p 9734 line 3: "... implementation **of** the newly implemented..."
- typo p. 9736 line 8: Figure 12 (not 13) should be referred to here
- typo p. 9736 line 19: insert "they" before "reach values"
- typo p 9737 line 3: Figure 14 (not 12) should be referred to here
- typo p 9738 line 21: "... of **the** simulated ~~the~~ GLYOX/MGLYOX..."

Additional references (not resuming references in the manuscript)

Crouse, J.D., Paulot, F., Kjaergaard, H. G., Wennberg, P. O., <http://www.rsc.org/suppdata/cp/c1/c1cp21330j/addition.htm> Additions and Corrections to "Peroxy radical isomerization in the oxidation of isoprene", Phys. Chem. Chem. Phys. 2011, 13, 13607. Amendment published 6th September **2012**

Crouse, J. D., Teng, A., Wennberg, P. O., Experimental constraints on the distribution and fate of peroxy radicals formed in reactions of isoprene + OH + O₂, ACM Meeting, Davis, CAL, Dec. **2014**

Dibble, T. S., Cyclization of 1,4-OH-carbonyls is not a homogeneous gas phase process, Chem. Phys. Lett. **2007**, 447, 5-9

Nguyen, V. S., Peeters, J., Fast (E)–(Z) Isomerization Mechanisms of Substituted Allyloxy Radicals in Isoprene Oxidation, J. Phys. Chem. A, web-published 5 Feb. **2015**, DOI: 10.1021/jp512057t