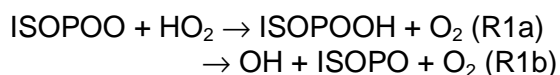


Review of Production of methyl vinyl ketone and methacrolein via the hydroperoxyl pathway of isoprene oxidation by Liu et al.

Referee Terry J. Dillon

The paper presents interesting results concerning clean-air isoprene oxidation. Experiments were conducted in conditions where the dominant fate of organic peroxy radicals (RO_2) is reaction with HO_2 . The authors have observed formation of small but significant yields of methacrolein (MACR) and methyl vinyl ketone (MVK), and present a convincing argument that these products result from radical recycling chemistry. Specifically, an OH yield of 7 % is derived for the reaction (R1) of HO_2 with the various isomeric RO_2 derived from isoprene (ISOPOO).



Two of the ISOPO products are known to decompose to form MVK and MACR, with concurrent production of HO_2 , hence detection of MVK or MACR from isoprene in such (NO_x free) conditions may be used as evidence for OH production in (R1). In reporting MVK, MACR, OH and overall HO_x yields following R1, the paper contains data and implications of considerable value to the atmospheric science community. However, some corrections and clarifications are required prior to publication in ACP, in particular regarding the distribution of ISOPOO available to react with HO_2 , and the quoted uncertainties in the reported MVK, MACR and HO_x yields.

In the introduction to $HO_2 + RO_2$ chemistry (page 3 line 52) it is stated that OH productions "has been demonstrated in the laboratory only for carbonyl-bearing RO_2 ". This is not quite the case. The only direct detection of OH was in the Dillon & Crowley study, and there only for carbonyl RO_2 . However, Jenkin and co-workers have shown that OH is produced in reactions of HO_2 with two RO_2 without carbonyl substitution, $HOCH_2O_2$ (Jenkin et al. 2007) and $CH_3OCH_2O_2$ (Jenkin et al. 2008).

The authors have taken care to design experiments where the production of MVK & MACR can be confidently attributed to $ISOPOO + HO_2$ (R1). A number of tests were carried-out to quantify / eliminate alternative chemistry leading to MVK & MACR. Nonetheless, I feel there are several points in the manuscript where further discussion and quantification of possible errors in MVK & MACR yields is necessary:

In sections 2, 3.1 & 3.6 a low temperature trap is mentioned. This is used to remove interference from low-volatility products ISOPOOH and IEPOX in the detection of MVK and MACR. Sensitivities to isoprene, MEK & MACR were unchanged, indicating that these compounds were not trapped. Can you quantify how efficient the trap was at removing ISOPOOH and IEPOX? This is crucial for assessing how much MEK and MACR were really derived from R1.

On page 3333 yields of MEK and MACR are derived via equation 2. This section is confusing, as rate coefficients k_1 & k_2 here do not correspond to the reactions R1 and R2 from the text, but instead to reactions of OH with isoprene and MVK. Please write out these reactions explicitly, and re-number them so that k_1 corresponds to R1, k_2 to R2 etc. In the text below I use k_1 to refer to the rate of $ISOPOO + HO_2$ (R1 in the manuscript text).

Also in equation 2, a wall-loss rate of 0 s^{-1} is reported. Could you be more precise regarding this parameter? No mention is made of wall-loss rates for radicals OH, HO_2 or ISOPOO. Are these important, or taken into account in this analysis? I note that for HO_2 levels of 540 ppt, and using $k_1 = 1.7 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ a first-order rate for (R1) of $k_1[HO_2] \approx 0.2 \text{ s}^{-1}$ may be derived, so even small losses of ISOPOO elsewhere (eg. near 0 s^{-1} to the wall or by

photolysis) may be important. That the lifetime of ISOPOO is of the order of a few seconds is important – see the comments on Table 3 and on Figure 1 below.

Was other unwanted photochemistry important? I could find no mention of the lamp output save reference on page 33328 “Within the CMFR, photolysis of H₂O₂ by ultraviolet light produced OH radicals, initiating isoprene oxidation” and from section 2.4 “The one-sun photolysis rates of the MCM model were scaled by 0.3 to match the lower light intensity of the HEC.” Nonetheless, lamps suitable for H₂O₂ photolysis would impact on other species, notably, MVK, MACR and perhaps isoprene. On page 33335 experiments conducted with different residence times are discussed. These are taken to indicate that photolysis of ISOPOOH & IEOPX are unimportant, though the experiment conducted at longer residence time did result in larger yields of MVK & MACR. The MCM provides photolysis rates, or at least coarse estimates, for ISOPOOH. Could you use your model output to quantify for experiment #1 how much chemistry was initiated by OH, how much by photolysis of other species (MVK, MACR, isoprene, ISOPOOH)? This sort of detail is important when, ultimately, your conclusions depend on precise determinations of quite small MVK and MACR yields.

Another potential interfering source of MVK and MACR products is the presence of small amounts of NO. The authors have taken every measure to minimise NO experimentally, and recorded (below detection limit) values of < 70 ppt. In section 3.3 & table 3 the proportion of ISOPOO reacting with HO₂, with NO and with itself is reported. A value of > 93 % was calculated for ISOPOO reacting with HO₂, with the remainder (< 7 %) reacting with NO. These calculations used literature values for rate coefficients (*k*) that are highly uncertain. For example, *k*₁ was obtained from the IUPAC database, based on the sole available measurement of *k*₁, from Boyd et al. (2003).

Consequently, a large uncertainty of $\Delta\log(k_1) = 0.3$, or approximately a factor of two is quoted by IUPAC. There is also some uncertainty in *k* for ISOPOO + NO, and the value of [HO₂] taken from your MCM simulations. Based on the upper-limit of 70 ppt for NO, and reported uncertainties in the rate coefficients for ISOPOO with HO₂ and NO I have calculated a lower-limit of 85 % for ISOPOO reacting with HO₂. How does this smaller lower-limit propagate into overall uncertainties in MVK, MACR & HO_x yields?

In table 3 and the text regarding the fate of ISOPOO, the unimolecular rearrangement proposed by Peeters et al. has been neglected. There is considerable dispute as to the importance of this process, with the 2009 Peeters calculations reporting a rate of around 1 s⁻¹, and Crouse et al. (2011) subsequently deriving a value of 0.002 s⁻¹ from experimental observation. Nonetheless, it is surely worth noting this controversy given the rate for (R1) of $k_1[\text{HO}_2] \approx 0.2 \text{ s}^{-1}$ in experiment #1 in this work.

My primary concern with this paper is that the uncertainties reported for MVK, MACR and HO_x yields are extraordinarily small. Very little detail is given about how such uncertainties were estimated. The supplemental info gives two short paragraphs describing error analysis using a Monte Carlo method. I would move this to the main text, and include more detail with numerical examples in an extended supplemental info. Please state in the main text whether uncertainties are 1 or 2σ. Please give some idea as to whether these are principally derived from data scatter, or from systematic errors in the experiment (calibrations etc.) or the documented uncertainties in literature parameters. Without a more detailed treatment of errors the reader simply cannot assess how robust these results really are.

I appreciate that the determinations of MVK & MACR concentration were of high precision. Nonetheless, from the data presented in Table 1 these were not insignificant, eg. for experiment #1 at steady-state (1.3 ± 0.1) ppb for MVK and (0.8 ± 0.1) ppb for MACR. Product yields were determined via equation 2 which contains terms such as rate coefficients, radical concentrations and wall-loss rates, resulting in yields for MVK of (4.6 ± 0.3) % and for MACR (3.2 ± 0.2) %. I would have expected the reported errors to increase as the calculations get

more complex and more uncertain parameters are included, but the opposite is the case here. How can this be justified? Ultimately a yield for HOx recycling of “15 ± 0.7%” is reported – uncertainty 1/20 of absolute value - even though this is dependent on the original MVK and MACR concentrations (precision ~ 1 / 10) and a whole host of other parameters in model simulations. As noted above (for k_1), some of these parameters are associated with large uncertainties. I can see that reliance on model simulation via the MCM is necessary, however where the results are dependent upon a critical parameter this should be highlighted, especially if data are in short supply. More discussion of assumptions made regarding the fate of ISOPOO is needed. As I see it, the yields reported in this work rely on results from Boyd et al. (2003) and Crouse et al. (2011) being substantially correct, and those of Peeters et al. (2009) being wrong. The reader should be left in no doubt about this.

Incidentally, the notation used for reporting uncertainty in yields throughout the manuscript is confusing. It may be best to clarify in the abstract that these are “percentage yields for MVK and MACR of 4.3 ± 0.4 and 3.2 ± 0.3 ” or include parentheses as I have above, eg. “(4.3 ± 0.4) % and (3.2 ± 0.3) %”. For the radical recycling yield I suggest you differentiate between an OH recycling yield of ~7 % and your overall HOx recycling yield (15 %). I also strongly suggest you revise upwards the uncertainty in these parameters.

Figure 1 displays isoprene oxidation pathways as reported by the MCM. My understanding is that these relative yields of ISOPOO A, B, C & D are the nascent or kinetic yields following O₂ addition, appropriate for conditions where the lifetime of ISOPOO is $\ll 1$ s. In polluted air, and in previous chamber experiments such yields are appropriate. However, Peeters et al. (2009) report that

“repetitive O₂ addition/elimination will continuously interconvert the three O₂-adduct isomers / conformers of a given OH-isoprene radical—leading to steadystate populations approaching equilibrium and so channel the bulk of the reaction flux through the fastest product forming route.”

Therefore in conditions of ISOPOO lifetime > 1 s, such as real clean-air, and also in your experiments, a different “equilibrium” distribution of ISOPOO applies. Please note that this equilibration of ISOPOO is not the controversial aspect of Peeters’ Leuven Isoprene Mechanism. For further reference see the discussion in Peeters et al. (2009), Peeters and Müller (2010), Nguyen et al. (2010), Crouse et al. (2011), and references therein.

Happily for the conclusions of this work, ISOPBOO (32 %, producing MVK) and ISOPDOO (60 %, producing MACR) dominate the equilibrium distribution. Peeters’ statement that the bulk of reaction proceeds via the fastest product route is redundant here providing that

- 1) the k_1 result from Boyd et al. (2003) applies to all ISOPOO, an assumption adopted in this work and in the MCM.
- 2) that the subsequent intramolecular rearrangements proposed by Peeters et al. (2009) do not apply, ie. are slower than reported. This assumption has also implicitly been applied when

Interestingly, if the equilibrium distribution and subsequent assumptions apply, then approximately a factor of two larger MACR than MVK yields would be expected. This was not observed from the experiments in this work. Does the observed ratio MVK:MACR of 4:3 from both the HO₂- and NO-dominated experiments provide evidence for a different equilibrium ISOPOO distribution? It is close to what would be expected from nascent / kinetic ISOPOO. Or are the larger MVK:MACR ratios reported in this work a result of secondary chemistry? It would be worth running a quick simulation using the Peeters rate constants for HO-ISOP + O₂ \leftrightarrow ISOPOO, and your experimental estimates of [HO₂] and [NO] to establish whether you are fully in the equilibrium regime in all experiments.

Finally, a few points concerning the atmospheric implications section, and Figure 2.

In the caption to Figure 2 it should be noted that unimolecular decomposition of ISOPOO may be important in unpolluted conditions, as proposed by Peeters et al. This is even if Crouse et al. are correct, and the unimolecular rate is slower than Peeters first reported. Crouse calculate up to 20 % of ISOPOO lost to the unimolecular process in rainforest conditions; 7-10 % globally, even using the much slower rate.

The final sentence “Another possibility, suggested by a recent report on instrumental issues, could be that the gap between measured and modeled OH was not so large as originally reported (Mao et al., 2012).” I see what you are getting at here, but apply caution, as it is hazardous to extrapolate from one set of campaign conditions to another. Or indeed from one instrument to another. However, it is worth noting that the paper by Mao suggests that OH was over-reported in some forest conditions. Strictly speaking the gap between measured and modeled OH was what it was; perhaps the gap between an ideal OH measurement and the model would not be (as) large, but we don't really know.

There is a rare typo on page 33326 line 6 “hyrotetroxide”.

References:

Boyd, A.A., Flaud, P-M., Daugey, M. and Lesclaux, R., Rate constants for $\text{RO}_2 + \text{HO}_2$ reactions measured under a large excess of HO_2 , *J. Phys. Chem. A*, 107, 818–821, 2003.

Crouse, J.D., Paulot, F., Kjaergaard, H.G. and Wennberg, P.O. Peroxy radical isomerization in the oxidation of isoprene., *Phys. Chem. Chem. Phys.*, 2011, **13**, 13607-13613, DOI: 10.1039/C1CP21330J

Jenkin, M. E., Hurley, M. D. and Wallington, T. J., *Phys. Chem. Chem. Phys.*, 9, 3149, 2007.

Jenkin, M. E., Hurley, M. D. and Wallington, T. J.: *Phys. Chem. Chem. Phys.*, 2008, **10**, 4274-4280

Nguyen, T.L., Vereecken, L., and Peeters, J., HOx Regeneration in the Oxidation of Isoprene III: Theoretical Study of the key Isomerisation of the Z-d-hydroxy-peroxy Isoprene Radicals., *Chem. Phys. Chem.* 2010, 11, 3996 – 4001

Peeters, J., Nguyen, T. L., and Vereecken, L.: HOx radical regeneration in the oxidation of isoprene, *Phys. Chem. Chem. Phys.*, 11, 5935–5939, doi:10.1039/B908511d, 2009.

Peeters, J. and Müller, J-F. Radical regeneration in isoprene oxidation via peroxy radical isomerisations. II: experimental evidence and global impact., *Phys. Chem. Chem. Phys.*, 2010, 12, 14227–14235 14227