

Authors' responses to referee and discussion comments on: Jenkin et al., Atmos. Chem. Phys. Discuss., 15, 9709–9766, 2015

We are very grateful to the referees and commenter for their contributions to the discussion, and for their generally supportive comments on this work, and on the MCM in general. We would also like to thank them for providing a series of particularly constructive and insightful comments, which are being used to produce a refined version of the mechanism and manuscript. We recognise that preparing those comments would have required considerable time and effort.

It is not always easy to ensure that publicly-available mechanisms such as the MCM are completely up to date, particularly for “fast-moving” topics such as isoprene degradation. Although not explicitly stated, the update described in the manuscript was based on an information cut-off of September 2014 (already extended to include the publication of Peeters et al., 2014), with the usual general requirement that the information had been peer-reviewed. The subsequent construction, testing and launching of the mechanism, and preparation of the manuscript, took from that time until the submission of the paper and release of the mechanism on 1st March 2015.

We note that several of the comments relate to information that was either only in the public domain shortly before the submission date, or has still not undergone peer-review now. Whilst it was impractical for us to have included this in the original mechanism, we are nonetheless very grateful for the guidance that these comments have provided, and are taking them into account in producing the refined mechanism.

The mechanism is thus being modified in relation to many of the review comments received and, where no change is being made, a discussion point related to the comment will be included or adjusted at the appropriate point in the revised manuscript in most cases (as also indicated below in relation to the specific comments). In preparing this response we have tested the effect of the changes on the first-generation product yields, and these are discussed and illustrated.

We anticipate that revision and re-launching of the mechanism will take about two months, and the refined mechanism will be made available as MCM v3.3.1. Revision of the idealised atmospheric simulations (i.e. Sect. 3) will be carried out over the same time period, such that a revised version of the manuscript should also be available in about two months.

Responses to the comments are now provided (the original comments are shown in blue font).

A. Comments by Jozef Peeters (Referee)

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.

Response: We are very grateful to the referee for recognising the progress made in implementing this extensive update to the MCM, including full representation of the LIM reaction framework reported by Peeters et al. (2009; 2014).

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.

Response: We thank the referee for providing such a clearly explained and justified set of comments, and for making these latest insights and interpretation available to us. We now respond to the specific comments in turn.

Comment A1: The rate coefficients for O₂ addition to the initial hydroxyl-isoprenyl adducts and for redissociation of the various resulting peroxy, denoted here as k(+O₂) and k(-O₂), 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(-O₂) of the Z-δ-OH-isoprenyl peroxy, the average is taken of the LIM1 k-values for the 1-OH-4-OO and 4-OH-1-OO peroxy (using the notations of Peeters et al., 2009 and in the footnotes of Table S1 of this work), and likewise for the k(-O₂) of the E-δ-OH-isoprenyl peroxy; for the k(-O₂) of the β-OH-isoprenyl peroxy 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(-O₂) to yield the cis- and trans-OH adducts. The k(-O₂) 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 peroxy. 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 ↔ 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: Keq1(1-OH-2-OO ↔ Z-1-OH-4-OO) = 1.8 × exp(-980/T), or Keq1(295) = 0.065; and Keq2(4-OH-3-OO ↔ Z-4-OH-1-OO) = 2.22 × 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 (Keq1 = 1.93 × exp(-1484/T) or Keq1(295) = 0.013; and Keq2 = 1.96 × 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-peroxy 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 ↔ Z-1-OH-4-OO and 1-OH-2-OO ↔ E-1-OH-4-OO reported by Crouse et al. at the ACM conference, Dec. 2014, agree with LIM1 within ± 30%. Since the steady-state populations f(Z-δ) of the isomerizing Z-δ-OH-peroxy — which together with the k(1,6-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-peroxy 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(-O₂) 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(Z-δ) for the 1-OH-peroxy at low k_{tr}.) The consequences of this will be discussed below.

Comment A2: The isomerization rate coefficient k(1,6-H) is assumed equal in the manuscript for the two peroxy Z-1-OH-4-OO and Z-4-OH-1-OO, and is derived from the experimental k(bulk) of Crouse et al. (2011) at k_{tr} = 0.021 s⁻¹, giving k(1,6-H) ≈ 0.10 s⁻¹ at 295 K. The reason for the low

value is simply the much too high population fraction $f(Z-\delta)$ of Z-1-OH-4-OO at this ktr, 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 ktr = 0.1 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 $k(1,6-H)$ 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 $k(1,6-H \text{ Z-4-OH-1-OO})/k(1,6-H \text{ Z-1-OH-4-OO})$ 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 ktr of ~ 0.01 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 ktr. This is because a major part of the 4-OH peroxy pool effectively isomerizes at low ktr, leaving little room for MACR production. (In fact, from this result one can derive that the total isomerisation yield at 295 K and ktr 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).

Comment A3: 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 K_{eq} 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 $k(+O_2)$ 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 $k(-O_2)$ were then found from $k(+O_2)/K_{eq}$. Given that the K_{eq} 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 $k(+O_2)$ and $k(-O_2)$ of LIM1, all calculated K_{eq} 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 $k(+O_2)$ and $k(-O_2)$ — by reducing both the $k(1,6-H)$ of LIM1 by a factor of 3, to become in the optimized LIM1b mechanism: $k(1,6-H \text{ Z-1-OH-4-OO}) = 1.3 \times 10^{(10)} \times \exp(-8591/T) \times \exp[10^{(8)}/T^{(3)}]$ s⁻¹ or 0.14 s⁻¹ at 295 K; and $k(1,6-H \text{ Z-4-OH-1-OO}) = 3.6 \times 10^{(10)} \times \exp(-8174/T) \times \exp[10^{(8)}/T^{(3)}]$ 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.)

Response: We thank the referee for this detailed and helpful explanation. The parameter amendments summarised in [Comments A1–A3](#) are being implemented into MCM v3.3.1, almost exactly according to the recommendations given.

We would initially like to explain our rationale for using structurally-averaged parameters previously. At the outset of the work we investigated using LIM1 exactly as presented in Peeters (2014). Fig. R1 below (broken lines) shows the corresponding calculated molar yields of selected first-generation products as a function of NO mixing ratio at 298 K. Although the performance is very impressive, there were some features that did not appear to be fully in accord with the wider database, suggesting that some modest optimisation was necessary. For example, the relative yields of MVK and MACR are consistently reported to be in the range 1.4–1.6, both at the high [NO] limit, and also at lower levels of [NO] (Karl et al., 2006; Liu et al., 2013) – with the exception of the recent study of Brégonzio-Rozier et al. (2015) that reports a ratio of 0.9. LIM1 predicts ratios increasing from about 1.6 at the high [NO] limit to a peak of 2.2 at around 1 ppb NO. In addition, the yield of unsaturated C₅ carbonyls is only 3 %, which is inconsistent with the value of (8.4 ± 2.4) % reported by Zhao et al. (2004), indicating that some adjustment to assumptions regarding the minor channel chemistry was also required.

Noting that LIM authors had themselves previously used geometric averages of $k(1,5\text{-H})$ for ISOPBO₂ and ISOPDO₂ and of $k(1,6\text{-H})$ for CISOPAO₂ and CISOPCO₂ to address issues related to MVK/MACR ratios (e.g. Peeters and Müller, 2010; Stavrakou et al., 2010; Tarraborelli et al., 2012), we found we were able to improve the calculated MVK/MACR by using structurally-averaged parameters, and by the optimising procedures and minor channel assumptions described in Sects. 2.1.4 and 2.1.1 of the original manuscript and in the SI (e.g. involving small adjustments to the initial addition ratios), leading to the result shown in Fig. 4 of the original manuscript. This had the main advantage of maintaining an approximately constant relative yield of MVK and MACR over the [NO] range of the studies reported in Table S2 of the SI, consistent with the results of those studies. We had also hoped that the structural averages might provide the initial basis for assigning parameters to similar structures formed in other systems, and also make the subsequent development of more reduced

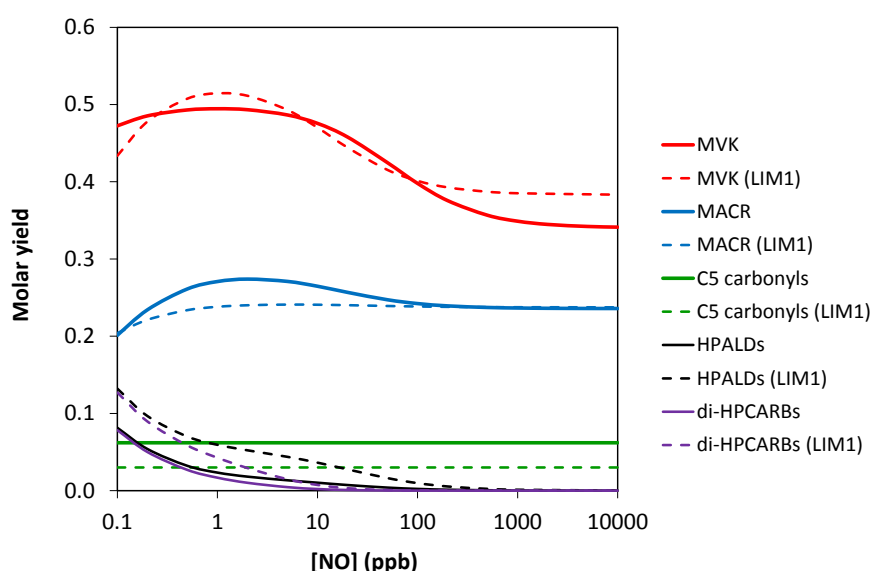


Figure R1: Molar yields of selected first-generation products of the OH-initiated oxidation of isoprene as a function of NO mixing ratio, at 298 K (N.B. the displayed [NO] range corresponds to the approximate k_{tr} range 0.02 – 2000 s⁻¹). The broken lines show those calculated with LIM1, as reported by Peeters et al. (2014). The full lines show those calculated with the refined MCM v3.3.1, taking account of [Comments A1–A3](#) above and with the additional optimisation described in the associated response.

representations more straightforward. However, we accept that the averaging procedure was not entirely appropriate, and are no longer using structurally-averaged parameters for $k(+O_2)$ and $k(-O_2)$, or for $k(1,5-H)$ or $k(1,6-H)$ for the H-shift isomerisation reactions of CISOPAO2, ISOPBO2, CISOPCO2 and ISOPDO2 in MCM v3.3.1.

We have tested the use of the LIM1 values of $k(+O_2)$ and $k(-O_2)$, scaled by a factor of 5 (as recommended in [Comment A3](#) by the referee), in conjunction with the other (relatively minor) optimisation procedures outlined in Sects. 2.1.1 and 2.1.4 of the original manuscript and in the SI. The corresponding [NO]-dependences of the yields of selected first-generation products are also shown in Fig. R1 (full lines). This incorporates re-optimised addition ratios of 57.6, 4.2, 4.2 and 34.0 % at positions 1, 2, 3 and 4, leading to a relative yield of MVK and MACR of 1.45 at the high [NO] limit. Similarly to the results with LIM1, this also results in an increase in MVK/MACR to a (lower) value of about 1.8 at about 1 ppb NO, and MVK yields of about 50 %, which are not consistent with the observations of Karl et al. (2006), who reported a yield ratio of about 1.5 with an MVK yield of (41 ± 3) % at about 0.2 ppb NO; or those of Liu et al. (2013) who reported a yield ratio of about 1.4 with an MVK yield of (41.4 ± 5.5) % at about 9 ppb NO. Based on the referee's recommendation, we are nevertheless applying this representation in MCM v3.3.1, to allow the revised mechanism to be consistent with the features described in [Comments A1–A3](#), which it does indeed recreate very well, (e.g. relative yields of C5HPALD1 and C5HPALD2), along with a number of other observables reported by Crouse et al. (ACM, 2014) (e.g. the nitrate ratios in the response to [Comment B1](#), below). However, we will necessarily need to discuss the discrepancies outlined above in the revised manuscript, which was not previously required for the structurally-averaged parameters used in MCM v3.3.

The values of $k(1,5-H)$ used for ISOPBO2 and ISOPDO2 in the refined MCM v3.3.1 are the LIM1 values reported in Peeters et al. (2014). For the 1,6 H shift reactions of CISOPAO2 and CISOPCO2, the optimisation procedure outlined previously in Sect. S1.4 was repeated, leading to the amended version of Fig. S4, shown as Fig. R2 below. Once again, the values of $k(1,6-H)$ were scaled to give a

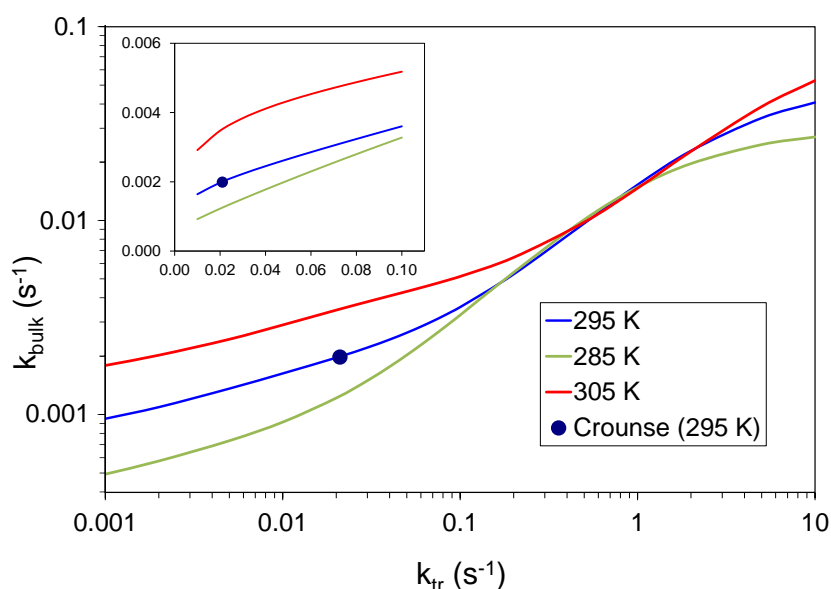


Figure R2: Variation of the phenomenological bulk isomerisation rate to form C5HPALD1 and C5HPALD2 (k_{bulk}) with the peroxy radical loss rate through “traditional” bimolecular reactions (k_{tr}), as calculated with the refined MCM v3.3.1 scheme at 285 K, 295 K and 305 K. The 295 K measurement reported by Crouse et al. (2011), as used to optimise the chemistry, is also shown (N.B. The presented values of k_{bulk} specifically represent only the assigned 50 % of the isomerisation reactions that form C5HPALD1 and C5HPALD2, such that the total effective isomerisation rates are the presented values multiplied by two).

value of $k_{\text{bulk}} = 0.002 \text{ s}^{-1}$ at $k_{\text{tr}} = 0.021 \text{ s}^{-1}$ (Crouse et al., 2011). In order to achieve this, we find that it is actually necessary to reduce the LIM1 values of k(1,6-H) by a factor of about 5, resulting in:

$$k(1,6\text{-H CISOPAO2}) = 7.33 \times 10^9 \times \exp(-8591/T) \times \exp[1.027 \times 10^8/T^3] \text{ s}^{-1} \text{ or } 0.090 \text{ s}^{-1} \text{ at } 295 \text{ K.}$$
$$k(1,6\text{-H CISOPCO2}) = 2.20 \times 10^{10} \times \exp(-8174/T) \times \exp[1.000 \times 10^8/T^3] \text{ s}^{-1} \text{ or } 1.0 \text{ s}^{-1} \text{ at } 295 \text{ K.}$$

These values are therefore about a factor of 1.6 lower than the "LIM1b" values quoted by the referee in [Comment A3](#). In all other respects, the updates in MCM v3.3.1 are exactly according to the recommendations given by the referee in [Comments A1–A3](#).

As pointed out by the referee at the end of [Comment A2](#), the revised representation does indeed result in a value of k_{bulk} at $k_{\text{tr}} \approx 4$ that is approximately a factor of 3 higher than with our previous structurally-averaged representation, and also contributes to the improvement in the simulated relative yields of C5HPALD1 and C5HPALD2.

Comment A4: 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 $\sim 10^7 \text{ s}^{-1}$. 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 .

Response: We are grateful to the referee for raising some mechanistic points that are relevant to previously reported first generation formation routes for the C₄ hydroxycarbonyl, hydroxymethacrolein (HMACR) (represented to be formed from ISOPAO), and 3-methylfuran (M3F) (represented to be formed from CISOPAO and CISOPCO). As justified further below, we have provisionally decided to leave the (relatively minor) chemistry of these oxy radicals unchanged until further information is available in the literature; although the points raised by the referee will be reflected in the discussion in the revised manuscript.

As indicated by the referee, the recommendations in [Comment A4](#) would completely remove the formation routes to these products, resulting in the alternative generation of C₅ hydroxycarbonyls. In practice, these routes have relatively minor impacts on the mechanism, and were included at least partially to account for the reported generation of HMACR and 3-methylfuran as minor products in

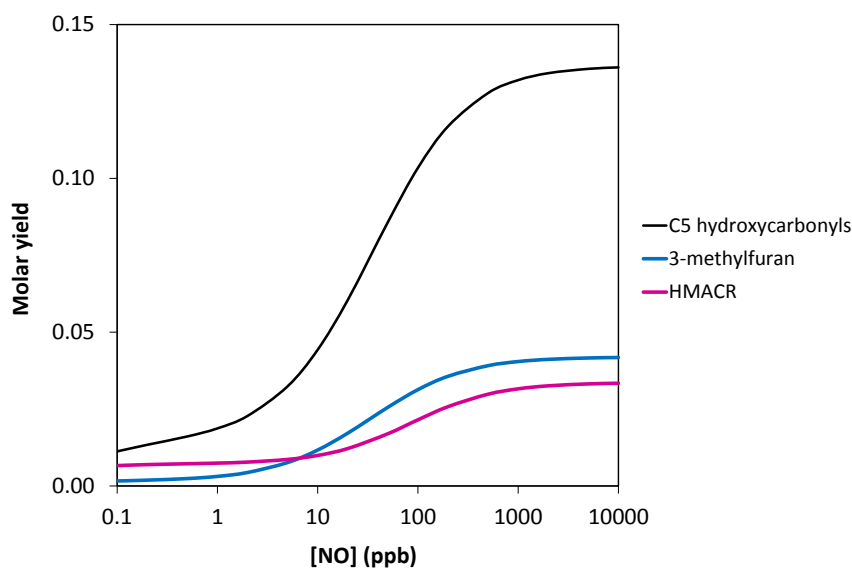


Figure R3: Molar yields of selected first-generation products of the OH-initiated oxidation of isoprene as a function of NO mixing ratio, at 298 K, as calculated with the refined MCM v3.3.1, taking account of [Comments 1–3](#) above and with the additional optimisation described in the responses to [Comments A1–A4](#).

chamber studies performed at the high [NO] limit. Fig. S3 above shows the calculated [NO] dependences of their molar yields, using the MCM v3.3.1 scheme refined as described in the previous response and with the oxy radical routes re-optimised following the procedure described in Sect. 2.1.4 of the original manuscript and in the SI – with the results being similar to those for MCM v3.3, presented in Fig. 4 of the original manuscript. This results in respective yields of 4.2 % and 3.3 % for 3-methylfuran and HMACR at the high [NO] limit, with the yields decreasing substantially for atmospheric conditions. Removing these routes would therefore have limited consequences and it can be argued that they therefore do not really class as “required major revisions”.

Other than re-optimising the system to the high [NO] yields, we have made no other changes to the mechanism in relation to the fates of these oxy radicals at the present time (as indicated above). This is so that routes to the formation of HMACR and 3-methylfuran as minor products remain in MCM v3.3.1, consistent with their reported formation in the chamber studies listed in Table S2.

Although the importance of its formation route was not specifically optimised, the retained chemistry for ISOPAO results in a yield of 3.3 % for HMACR which is in excellent agreement with the C₄ hydroxycarbonyl yield of (3.3 ± 1.6) % reported by Zhao et al. (2004). However, we will point out in the revised manuscript that the retention of its formation chemistry is not supported by the very recent results of Nguyen and Peeters (2015) (published shortly before submission of our manuscript).

The retained chemistry for CISOPAO and CISOPCO results in an optimised high [NO] yield of 3-methylfuran of 4.2 %, which is based on the results of Atkinson et al. (1989), Paulson et al. (1992) and Ruppert and Becker (2000), who reported respective yields of (4.4 ± 0.6) %, (4.0 ± 0.2) % and (4.0 ± 1.4) %. It is also noted that the recent study of Brégonzio-Rozier et al. (2015) reported a yield of (3.3 ± 1.6) % at intermediate [NO] mixing ratios, which is also consistent with our representation.

The referee argues that 3-methylfuran is likely formed as a product of heterogeneous reactions of the C₅ hydroxycarbonyls, citing support from the theoretical work of Dibble (2007) and the failure of Sprengnether et al. (2002) to detect 3-methylfuran under near wall-free conditions – and we agree

that there is some uncertainty here. However, it should also be noted that Sprengnether et al. (2002) actually report an upper limit yield of 2 % at 750 Torr, suggesting that the yields reported in other studies were already close to their detection limit. In addition to this, Atkinson et al. (1989) found that the yield was independent of a systematic ten-fold change in the reactor volume, and the yields reported in the other studies cited above are remarkably consistent, despite differences in reactor sizes, surface types and processing times. Its formation profile has also been reported to be consistent with formation as a first-generation product (Atkinson et al., 1989; Benkelberg et al., 2000; Lee et al., 2005), which would not be observed if it was generated solely from (heterogeneous) reactions of other first-generation products (i.e. the C₅ hydroxycarbonyls). In this respect, however, Lee et al. (2005) reported evidence for both a prompt and delayed source of 3-methylfuran at 323 K, possibly consistent with both mechanisms operating. These studies are therefore consistent with a gas phase formation route for 3-methylfuran, such as that proposed by Francisco-Márquez et al. (2003) and applied here. However, as indicated above, we agree that there is some uncertainty in the sources of 3-methylfuran, and we will include some discussion of this uncertainty in the revised manuscript.

As shown in Fig. R3, the re-optimised chemistry results in a yield of the C₅ hydroxycarbonyls of 13.6 % at the high [NO] limit, which is a slight increase from the value of 11.3 % with the original MCM v3.3 scheme. This revised value is consistent with the reported yields of (19.3 ± 6.1) % (Zhao et al., 2004), ~15 % (Baker et al., 2005) and ~10 % (Paulot et al., 2009). Inclusion of the changes indicated by the referee would have increased the C₅ hydroxycarbonyl yield to about 21 %, with formation of HMAcR and 3-methylfuran reduced to zero.

Comment A5: 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”.

Response: We referee raises a valid point, and we apologise for overlooking this relevant information and discussion in Peeters and Nguyen (2012). The text in Sect. 2.1.4 will be amended accordingly in the revised manuscript.

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).

Response: The discussion at this point in the manuscript is referring to the formation of MACR, HCHO and HO₂ from the chemistry of the β -hydroxy-oxy radical, ISOP34O, and we assume the referee is therefore referring to the chemistry of this species, rather than that of the precursor peroxy radical, ISOP34O2. The decomposition of β -hydroxy-oxy radicals to form a carbonyl and an α -hydroxyalkyl radical, followed by reaction of the α -hydroxyalkyl radical with O₂ to form a second carbonyl and HO₂ is (of course) a very well established process, and is standard in most mechanisms. It was, for example, included for ISOP34O in the isoprene mechanisms presented by Tuazon and Atkinson (1990) and Jenkin and Hayman (1995), with a decomposition rate of about 2 x 10⁶ s⁻¹ estimated for this type of structure by Atkinson (1997). We may have misunderstood the point the referee is making, but cannot see how the information in Peeters et al. (2014) builds upon previous knowledge this for this specific structure.

- 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...”.

Response: We thank the referee for pointing this out. The text in the revised manuscript will be amended accordingly.

- 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).

Response: We named these species this way because they are MVK and MACR with two hydroperoxy groups added to the double bond in each case, and such nomenclature is consistent with species such as dihydrofurans (for example). However, we accept that this is not entirely conventional for oxygenated substituents, and will rename the species as DHPMEK (i.e. with a methylethyl ketone base frame) and DHPMPAL (i.e. with a methylpropanal base frame) in MCM v3.3.1.

The text at this point in the manuscript is describing the optimisation and performance of the mechanism already presented in more detail on lines 6-28 on page 9715, where the chemistry is fully attributed to Peeters et al. (2014) and Crouse et al. (2011). However, we will include the citations again to reinforce this point. We were unaware of the “Addition and Correction” amendment of Crouse et al. (2012), and are grateful to the referee for alerting us to it. This will be cited accordingly in the revised manuscript.

- 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...”

Response: We thank the referee for identifying these typographical errors, which will be corrected in the revised manuscript.

B. Comments by J.-F. Müller

Opening comment: This article is important as it presents a quite comprehensive mechanism for isoprene which will surely be widely disseminated and used in the community interested by the impact of isoprene. Given the large number of reactions involved, it is to be expected that many issues, questions and problems remain, in spite of the impressive work which has been done to incorporate the recent relevant mechanistic updates. Besides the points raised by Jozef Peeters, I

have the following remarks which I hope can contribute to improve the manuscript and possibly the mechanism.

Response: We thank J.-F. Müller for the supportive comments on the MCM, and for recognising the magnitude of the task in providing this update. We are also grateful to him for contributing to the discussion and for providing a series of helpful and constructive comments, which we now respond to in turn.

Comment B1: p. 9720 and Fig. 5 : The 1st generation nitrate yields in MCMv3.3 follow more or less an average of different experimental studies. Note that in atmospheric conditions (relatively low NO), two isomers are largely dominant: ISOPN-1,2 (ISOPBNO₃) and ISOPN-4,3 (ISOPDNO₃). But the MCM assumes a twice higher nitrate yield (14% vs 7%) for the ISOPDO₂+NO reaction than for the ISOPBO₂+NO reaction. This is in line with the experimental study of Lockwood et al. But very serious doubts can be raised regarding the Lockwood et al. results since it provided a completely wrong determination of the ozonolysis rate constant for the 1,2 nitrate : $10^{-16} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ i.e. a factor of 20-40 above the experimental value determined by Lee et al. 2014 for the very similar 4,3 nitrate. This suggests a wrong identification of the different isomers by Lockwood et al. in particular for the 1,2 isomer. Therefore I would recommend ignoring the Lockwood results in this context, and adopting identical nitrate yields for 1,2 as for 4,3.

Response: The referee raises a number of interesting points. The relative magnitudes of the yields of the major hydroxynitrates from the corresponding peroxy radicals were actually unchanged from those used in several earlier versions of the MCM. These reflected the traditional view that the formation of secondary nitrates was believed to be strongly favoured over primary or tertiary ones (e.g. Carter and Atkinson, 1989; Lightfoot et al., 1992), although based on a very sparse dataset for tertiary peroxy radicals. As indicated, the resultant calculated distribution with MCM v3.3 matches that reported by Lockwood et al. (2010) quite well, and that study therefore provided some support for the representation. However, we recognise that there is a lot of uncertainty here, with other studies reporting substantially different distributions (Giacopelli et al., 2005; Paulot et al., 2009). In addition, the recent study of Teng et al. (2015) suggests that the yields of hydroxynitrate formation follow a trend of primary < secondary < tertiary, for isomeric peroxy radicals, which challenges the traditional view (as also previously raised by Orlando and Tyndall, 2012).

We agree that the ozonolysis rate coefficient reported by Lockwood et al. (2010) for ISOPBNO₃ is likely erroneous, and this was not used in MCM v3.3 (see also the response to [Comment B3](#) below) – although the isomer identification procedure in their paper appears logical and well-justified. In practice, their reported rate coefficient for $k(\text{O}_3 + \text{ISOPBNO}_3)$ seems to be too high for any of the hydroxynitrate isomers, such that it may alternatively be that there was a complication in the kinetics experiment rather than in species identification. The results of the other studies (Giacopelli et al., 2005; Paulot et al., 2009) are also counterintuitive in some respects, in that they report particularly important contributions from the primary δ -hydroxy nitrates ISOPCNO₃ and/or ISOPANO₃. Based on this, Paulot et al. (2009) derived hydroxynitrate yields of 24 % from the reactions of NO with the primary δ -hydroxy peroxy radicals (ISOPAO₂, ISOPCO₂, CISOPAO₂ and CISOPCO₂) and 6.7 % from the reactions of NO with the secondary β -hydroxy peroxy radical (ISOPDO₂) and the tertiary β -hydroxy peroxy radical (ISOPBO₂); where each peroxy radical also possesses an “allyl” functionality. Given the results of Teng et al. (2015) for (albeit simpler) hydroxyperoxy radicals, a yield ratio of 3.6 for primary/secondary and primary/tertiary is clearly unexpected on the basis of published trends.

In view of J.-F. Müller’s comment, and the above considerations, we have applied an adjusted methodology in MCM v3.3.1. As suggested, we have assumed that the branching ratios for nitrate

formation are equivalent for the β -hydroxy peroxy radicals, ISOPBO2 (tertiary) and ISOPDO2 (secondary); but have applied 20 % lower nitrate yields for the primary δ -hydroxy peroxy radicals (ISOPAO2, ISOPCO2, CISOPAO2 and CISOPCO2), to reflect the well-established lower propensities of primary peroxy radicals to form nitrates (e.g. Carter and Atkinson, 1989), which is also supported by

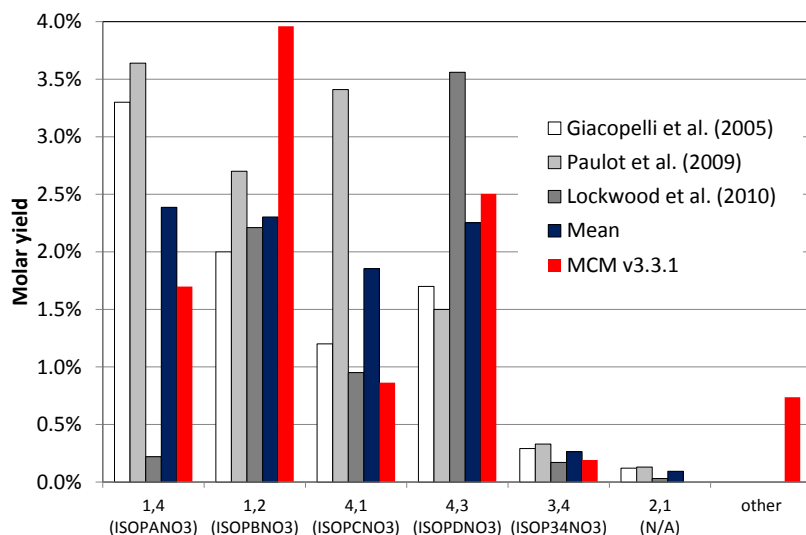


Fig. R4: Reported molar yields of speciated nitrate products formed from the first-generation OH-initiated oxidation of isoprene. The “1,4” and “4,1” categories include contributions from both *E*- and *Z*- isomers, where reported. The MCM v3.3.1 values correspond to 298 K at the high [NO] limit, with the total yield being 10 %. The “other” category includes C524NO₃ (formed in the mechanism to HMA CR formation), C526NO₃ (formed in the mechanism to methyl glyoxal/glycolaldehyde formation) and C527NO₃ (formed in the mechanism to glyoxal/hydroxyacetone formation). The “2,1” isomer is not formed in MCM v3.3.

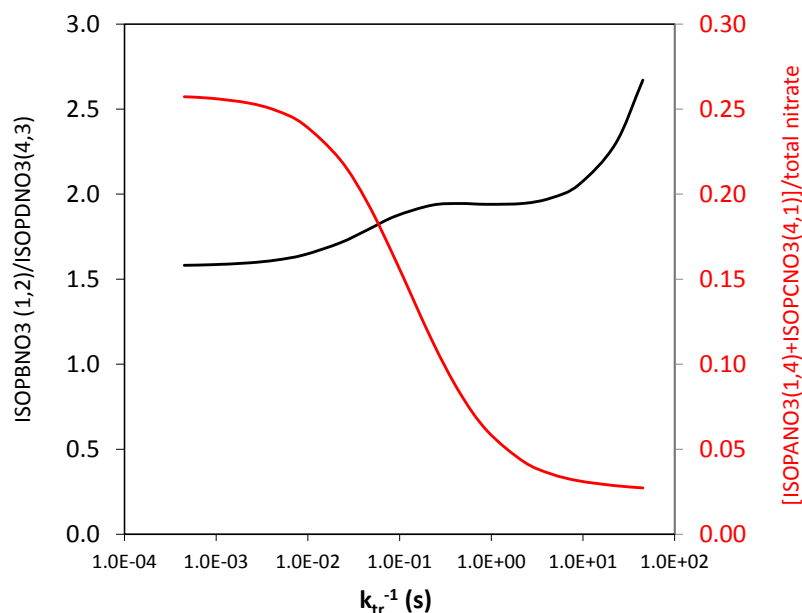


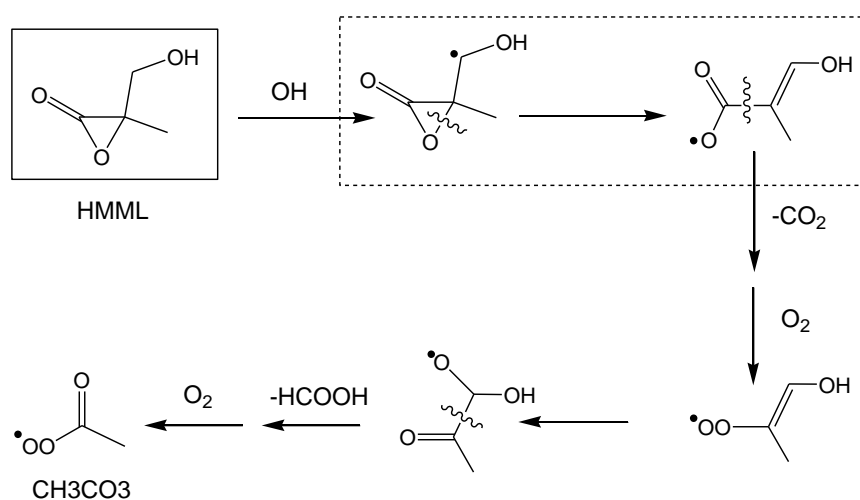
Fig. R5: Variation of first generation nitrate ratios with the reciprocal of the peroxy radical loss rate through “traditional” bimolecular reactions (k_{tr}^{-1}), as calculated with the refined MCM v3.3.1 scheme; where the “high [NO]” limit corresponds to the limiting values at low k_{tr}^{-1} . The black trace is the ratio of the β -hydroxynitrate isomers; the red trace is the fractional contribution of the δ -hydroxynitrate isomers to the total first generation nitrates.

the recent work of Teng et al. (2015) for hydroxyperoxy radicals. Following re-optimisation of the total first generation nitrate yield to 10 %, this results in a nitrate-forming branching ratio of 10.4 % for ISOPBO2 and ISOPDO2; and of 8.7 % for ISOPAO2, ISOPCO2, CISOPAO2 and CISOPCO2. The resultant distribution (shown in Fig. R4 above) does not really match any of the previously reported distributions, reflecting the lack of a consensus. However, the representation does seem to recreate quite well the total fractional contribution δ -hydroxy isomers, and the relative contributions of the two β -hydroxy isomers reported recently by Crouse et al. (ACM, 2014), and their dependence on k_{tr} , as shown in Fig. R5 .

Comment B2: p. 9722-9723 : In the MCM reaction file, the reaction of HMML with OH produces CH3CO3 + HCOOH. I guess the MCM protocol was followed here, but given the recent interest in the atmospheric sources of formic acid, it would be worthwhile to provide some more details on how these products are formed.

Response: Although HMML is proposed to play a role in SOA formation mechanisms, it is nonetheless a relatively minor product of the gas phase chemistry (i.e. partially produced from the reactions of OH with MPAN and MACO3H), which is expected to undergo efficient reactive uptake on acidic aerosol particles to form condensed phase 2-methylglyceric acid. Noting that some published representations do not declare any products of the reaction of OH with HMML (e.g. Lin et al., 2013), the aim for HMML and other minor products in the MCM is to provide a simplified representation of their degradation chemistry. Without such measures, the isoprene scheme would potentially proliferate to $\sim 10^4$ species (e.g. Aumont et al., 2005).

The following schematic shows the (notional) mechanism leading to the represented products, HCOOH and CH3CO3 (note that CO₂ is not declared):



SAR methods predict an OH rate coefficient of $4.33 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, with > 90 % attack at the -CH₂OH group. This was therefore assumed to be exclusive. The boxed chemistry is analogous to that proposed for the epoxydiol, IEPOXB, by Bates et al. (2014) - but avoids the minor channel that would form a further new species (formylmethyl lactone), to limit the proliferation of minor chemistry. The subsequent chemistry remains based on rules described in the original MCM protocol (Jenkin et al., 1997), for which there are reported precedents. The acyloxy radical is assumed to decompose through loss of CO₂, leading to formation of a hydroxyvinyl radical (which is also one of the isomers that can be formed from OH + propyne). The subsequent reaction of the hydroxyvinyl radical with O₂ is assumed to produce HCOOH and CH₃CO₃, following the generic mechanism applied to vinyl-type radicals (Jenkin et al., 1997). The formation of HCOOH and acetyl radicals is well established for the reaction of OH with propyne (e.g. Yeung et al., 2005), and it is therefore

justifiable that this reaction produces HCOOH. However, we recognise that other product channels potentially also contribute, e.g. the formation of methylglyoxal and OH.

The point about atmospheric sources of HCOOH is a fair one. If reactive uptake of HMML is being represented which, as indicated above, is the main current interest of including HMML in mechanisms, the gas phase chemistry will be of diminished importance. Even without this, we suspect that the reaction of OH with HMML is sufficiently minor for other HCOOH sources to dominate (e.g. from the ozonolysis of isoprene and other biogenics). Nevertheless, will we introduce a second channel forming methylglyoxal and OH in the refined mechanism, and will examine the impact of the reaction on HCOOH formation in the revised idealised atmospheric simulations.

Comment B3: p. 9724, lines 4-5 : From the MCMv3.3 reaction file, $k(\text{ISOPDNO}_3+\text{O}_3) = 7 \cdot 10^{-19} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$, which is well above the range given by Lee et al. (2014) i.e. $(2.5-5) \cdot 10^{-19} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$. Is there a reason for that?

Response: We are pleased to have the opportunity of clarifying how the rate coefficients for the hydroxynitrates were assigned, as there is never enough room in publications to describe all the methods used in detailed mechanisms. The following reasoning was used:

(i) Independently of the present work, we are currently in the process of updating a SAR method for the reactions of O_3 with alkenes, within which the following reference rate coefficients have been defined (where R = alkyl) at 298 K, based on analysis of data for the reactions of O_3 with 40 acyclic monoalkenes: $k(\text{O}_3 + \text{CH}_2=\text{CHR}) = 1.0 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$; $k(\text{O}_3 + \text{CH}_2=\text{CR}_2) = 1.4 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$; $k(\text{O}_3 + \text{CHR}=\text{CR}_2) = 4.7 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$; with these values being similar to those reported elsewhere (e.g. Calvert et al., 2000).

(ii) A comparison of $k(\text{O}_3 + \text{prop-2-ene-1-ol}) = 1.8 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Le Person et al., 2009) with $k(\text{O}_3 + \text{CH}_2=\text{CHR})$ was used to infer an approximate substituent factor of $F(-\text{C-OH}) = 1.8$ for replacing “-R” with a “-C-OH” group on a double bond.

(iii) The values of $k(\text{O}_3 + \text{ISOPANO}_3)$ from the studies of Lockwood et al. (2010) and Lee et al. (2014) agree to better than a factor of 2. The rate coefficient for this reaction was therefore assigned an average value of $k = 4.1 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, based on those studies; with the same value also applied to $k(\text{O}_3 + \text{ISOPCNO}_3)$, because ISOPCNO₃ possesses the same base frame and substituents. A comparison of $k(\text{O}_3 + \text{ISOPANO}_3)$ with the value of $k(\text{O}_3 + \text{CHR}=\text{CR}_2)$, and taking account of the substituent factor for the “-C-OH” group, allows an approximate substituent factor of $F(-\text{C-ONO}_2) = 0.05$ to be inferred for replacing “-R” with a “-C-ONO₂” group on a double bond.

(iv) $k(\text{O}_3 + \text{ISOPBNO}_3)$ was assigned a value of $k(\text{O}_3 + \text{CH}_2=\text{CHR}) \cdot F(-\text{C-ONO}_2) = 5.0 \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, with the OH group assumed to be too remote to have an effect. As indicated by the commenter in **Comment B1**, this is about a factor of 200 lower than that reported by Lockwood et al. (2010), but comparable to the (lower limit) range $(2.6 - 5) \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, reported by Lee et al. (2014) for the structurally-similar isomer, ISOPDNO₃.

(v) $k(\text{O}_3 + \text{ISOPDNO}_3)$ was assigned a value of $k(\text{O}_3 + \text{CH}_2=\text{CR}_2) \cdot F(-\text{C-ONO}_2) = 7.0 \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, with the OH group assumed to be too remote to have an effect. This value is fully consistent with the (lower limit) range $(2.6 - 5) \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, reported by Lee et al. (2014).

Comment B4: p. 9725, on the photolysis of carbonyl nitrates : the photolysis rates of carbonyl nitrates in the MCM reaction file are given as the photorate of nitrooxy acetone multiplied by a scaling factor deduced from Table 3 in Müller et al. (2014), which is reasonable. For the β -nitrooxy

aldehydes, however, for which no photorates were presented in Müller et al. (2014), the MCM scaling factor is taken to be the same as for the β -nitrooxy ketones (0.91). Due to the much higher absorption cross sections of aldehydes compared to ketones, the scaling factor for β -nitrooxy aldehydes should be much higher. I estimate a factor of 4 using assumptions similar as for the other carbonyl nitrates. Note that MCM-type expressions of the photolysis rates can be derived for the carbonyl nitrates, based on a fit of TUV estimations at three zenith angles (0, 30 and 60 degrees). Based on such calculations (assuming 300 DU ozone), I obtain the following expressions:

$$J(\text{NO}_3\text{CH}_2\text{CHO}) = 2.119\text{E} - 04 \times (\text{COSX})^{0.672} \times \text{EXP}(-0.328/\text{COSX})$$

$$J(\text{MACRNO}_3) = 4.926\text{E} - 04 \times (\text{COSX})^{0.637} \times \text{EXP}(-0.312/\text{COSX})$$

$$J(\text{C58NO}_3) = 2.182\text{E} - 04 \times (\text{COSX})^{0.779} \times \text{EXP}(-0.378/\text{COSX})$$

$$J(\text{MVKNO}_3) = 8.949\text{E} - 05 \times (\text{COSX})^{0.799} \times \text{EXP}(-0.385/\text{COSX})$$

$$J(\text{HMKANO}_3) = 5.594\text{E} - 05 \times (\text{COSX})^{0.946} \times \text{EXP}(-0.454/\text{COSX})$$

where COSX is the cosine of the zenith angle, $\text{NO}_3\text{CH}_2\text{CHO}$ is ethanal nitrate, MACRNO_3 ($\text{OCHC}(\text{CH}_3)(\text{ONO}_2)\text{CH}_2\text{OH}$) is a model compound for most α -nitrooxy aldehydes, C58NO_3 ($\text{OCHCH}(\text{OH})\text{C}(\text{CH}_3)(\text{ONO}_2)\text{CH}_2\text{OH}$) a model compound for β -nitrooxy aldehydes, MVKNO_3 ($\text{CH}_3\text{C}(\text{O})\text{CH}(\text{ONO}_2)\text{CH}_2\text{OH}$) a model compounds for α -nitrooxy ketones, and HMKANO_3 ($\text{CH}_3\text{C}(\text{O})\text{CH}(\text{OH})\text{CH}_2\text{ONO}_2$) a model compound for β -nitrooxy ketones.

Response: We are grateful for these further insights into the photolysis rates of carbonyl nitrates. There has been limited guidance in the literature on how to treat the photolysis of multifunctional organic species in explicit mechanisms, and the MCM has necessarily largely assumed that chromophores act independently. The paper of Müller et al. (2014), in addition to those of Peeters et al. (2009; 2014), have therefore provided major advances in this area, which are invaluable to mechanism developers. We hope these authors will continue to extend coverage to other multifunctional species.

The recommended revised treatment of β -nitrooxy aldehydes will be applied in MCM v3.3.1. We are also grateful for the provision of the set of X-dependent expressions. With the exception of the β -nitrooxy aldehyde model, $J(\text{C58NO}_3)$, the corresponding values at 30 degrees are consistently about 20 % higher than our currently applied values, suggesting that a similarly derived expression for our reference photoreaction (the photolysis of nitro-oxy acetone) would also give a photolysis rate at 30 degrees that is about 20 % higher than the X-dependent expression that we currently use:

$$J(\text{NOA}) = 4.365\text{E}-05 \times (\text{COSX})^{1.089} \times \text{EXP}(-0.323/\text{COSX})$$

For simplicity in the short term, we will apply a new scaling factor for the photolysis of β -nitrooxy aldehydes, which we estimate to be 4.4, using the same procedure as previously (in agreement with that given in [Comment B4](#)). However, the protocol rules on which the MCM is based are in the process of being systematically revised. This will include an updated and expanded list of parameterisations for photolysis reactions, and we will adopt the methodology recommended above for carbonyl nitrate photolysis.

Comment B5: p. 9726-9727 : the oxidation mechanism of IEPOXB is largely based on the mechanism presented by Bates et al. (2014). However I note that the 1,5-H shifts of the peroxy radicals proposed by Bates et al. (their Fig. 7) were neglected in the MCM (Fig. 8). This might be very well justified, but I'm wondering on what basis those processes were neglected in the MCM.

Response: The major peroxy radicals formed from $\text{OH} + \text{IEPOXB}$ are C57O_2 and C58AO_2 , which account for 74 % of the reaction. The 1,5-H shift reactions of these peroxy radicals would be in direct

competition with 1,4-H shift reactions, as also proposed in Fig. 7 of Bates et al. (2014). The assigned rate coefficient for the 1,4-H shift reactions (about 0.6 s^{-1} at 298 K, based on that for the analogous α -formyl peroxy radical, MACRO2: Crouse et al., 2012) is about a factor of 100 faster than the rate coefficient estimated for the 1,5-H shift reaction of MACRO2 in the SI of Peeters et al. (2009) (0.005 s^{-1} at 298 K), such that the 1,5-H shift of C57O2 and C58AO2 cannot compete and need not be represented. It should also be noted that Peeters et al. (2014) subsequently revised down the Peeters et al. (2009) "preliminary estimates" of $k(1,5\text{-H})$ for ISOPBO2 and ISOPDO2 by a factor of about 5, suggesting that $k(1,5\text{-H})$ for MACRO2 may have been similarly overestimated by Peeters et al. (2009).

The reaction of OH with IEPOXB also generates a minor β -hydroxy peroxy radical, C59O2, with a 15 % yield. There have been no reported estimates of 1,5-H shift rate coefficients for structures analogous to C59O2. However, 1,5-H shift reactions are generally believed to be very slow for β -hydroxy peroxy radicals formed from simple monoalkenes (e.g. da Silva et al., 2010), and are not automatically represented in the MCM for β -hydroxy peroxy radicals, unless there is clear evidence that they are likely to contribute (e.g. as in the cases of the β -hydroxy *allyl*-peroxy radicals ISOPBO2 and ISOPDO2). The 1,5-H shift reaction of C59O2 is therefore also not represented. It should be noted that Fig. 7 in Bates et al. (2014) (quite justifiably and helpfully) outlines probable and possible routes to the observed products, for which there are often several potential sources included; but the authors did not claim to have proven the existence of all the routes presented.

Comment B6: p. 9729 lines 10-14: the compounds HVMK and HMAc are assumed to photolyze as MVK and MACR, respectively, which means that photolysis is simply negligible for those compounds in MCM, due to the known very low photolysis quantum yields of MVK and MACR. But HVMK and HMAc are ketone-enols, with highly specific properties due to H-bonding, very different from the simple unsaturated carbonyls MVK and MACR. As outlined in Peeters et al. (2014), and by analogy with the case of C2572 acetylacetone for which laboratory data is available, the ketone-enols are expected to photolyze into OH and a strongly stabilized radical at a rate of about $(2\text{-}3)\cdot 10^{-4} \text{ s}^{-1}$, assuming a quantum yield close to unity. The latter assumption is justified by the allowed type of transition and much lower wavelengths involved in the photodissociation of ketone-enols compared to the cases of MVK and MACR (forbidden transition). As a consequence, the photolysis of HVMK and HMAc should be far from being negligible. In the MCM reaction file, the photolysis of the nitrooxy enal NC4CHO ($\text{O}=\text{CHCH}=\text{C}(\text{CH}_3)\text{CH}_2\text{ONO}_2$) (formed in large amounts from the oxidation of isoprene by NO_3) generates as products C4MDIAL + HO2 + NO2, where C4MDIAL is the unsaturated dialdehyde $\text{O}=\text{CH}-\text{C}(\text{CH}_3)=\text{CH}-\text{CH}(\text{O})$. But if we assume that NC4CHO photolysis proceeds by NO_2 expulsion (as apparently assumed here), the oxy radical co-product is the same as the radical formed in the photolysis of C5HPALD2. We would therefore expect the same subsequent chemistry as outlined in Sect. 2.2.4 and Fig. 9.

Response: We are very grateful for these comments. As indicated, the information about the photolysis of HVMK and HMAc is very clearly stated in Peeters et al. (2014), but we somehow managed to overlook it. This will be rectified accordingly in the refined MCM v3.3.1, and these reactions will of course further supplement HO_x formation from the chemistry of the C5HPALDs.

As indicated, NC4CHO is formed specifically from the NO_3 -initiated oxidation, which was not revised in this update. However, we agree fully with the point made, and will revise the photolysis products as indicated in MCM v3.3.1.

Finally, we would like to reiterate our thanks to J.-F. Müller for contributing to the discussion, and for providing clear and helpful advice.

C. Comments by Referee 2

General comment: The manuscript describes the update of isoprene oxidation mechanism according to the significant advancements that have been made in the last few years. It is important because of the central role of isoprene in tropospheric chemistry and because of widespread use of MCM in the community as a reference.

Response: We thank the referee for the supportive comments on the MCM, and for recognising the value and timeliness of this update to the mechanism.

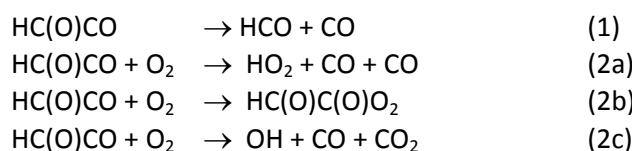
The description of the updates is detailed and clear although in some places it is still obscure how reaction products were assigned. The points raised by J. Peeters (reviewer) and J.-F. Müller need to be dealt with. In fact assuming the same rate constant for the 1,6-Hshift by CISOPAO2 and CISOPCO2 is against both the experimental and theoretical data. Below I list two other additional issues I found with this MCM update and a minor comment.

Response: We thank the referee for complimenting the clarity of the update description in our paper. This is always a compromise between providing enough information to make it clear what is included in the mechanism, without reproducing large amounts of information that are available elsewhere.

The referee raises a valid point about the description of the implementation of LIM reaction framework (Peeters et al., 2014), in that we did not explain why we had used structurally-averaged parameters. There was actually a clear precedent for doing this, in that even LIM authors themselves had previously used geometric averages of $k(1,5\text{-H})$ for ISOPBO2 and ISOPDO2 and of $k(1,6\text{-H})$ for CISOPAO2 and CISOPCO2 to address issues related to MVK/MACR ratios (e.g. Peeters and Müller, 2010; Stavrou et al., 2010; Tarraborelli et al., 2012). However, as discussed above in response to **Comments A1–A3**, we are no longer using geometric mean parameters for $k(1,5\text{-H})$ or $k(1,6\text{-H})$ in the refined MCM v3.3.1, and are now in line with the referee's view.

Comment C1: HCOCO chemistry. In which way has Lockhart et al. (2013) been taken into account if no prompt HCOCO* dissociation of 60% is implemented? Moreover, Da Silva (2010) reports a personal communication with J. Orlando correcting the Orlando and Tyndall (2001) estimate of HCOCO thermal decomposition rate constant that is half the originally published one. Instead of $1.4E12 \cdot \exp(-3160/\text{temp})$ it should be $7E11 \cdot \exp(-3160/\text{temp})$.

Response: As described in Sect. 2.2.5 of the original manuscript, the updated chemistry of the HCOCO radical took account of information reported in a number of studies, namely Orlando and Tyndall (2001), da Silva (2010) and Lockhart et al. (2013). The reaction framework presented by Orlando and Tyndall (2001), reactions (1), (2a) and (2b), was used as a convenient starting point for an atmospheric representation:



Reaction (2c) was added to reflect the OH forming route proposed by da Silva (2010), with OH yields subsequently characterised experimentally by Lockhart et al. (2013). The values of k_1 and k_{2a} were taken directly from Orlando et al. (2001). The value assigned to k_{2b} by Orlando and Tyndall (2001) (i.e. to the route that ultimately produced CO and CO₂ in their system) was divided between reaction

(2b) and the newly implemented reaction (2c). It was found that use of respective values of 0.24 and 0.76 for $k_{2b}/(k_{2b}+k_{2c})$ and $k_{2c}/(k_{2b}+k_{2c})$ resulted in an OH yield of 0.38 at 212 K, in agreement with that reported by Lockhart et al. (2013), and a value of 0.22 at 295 K in acceptable agreement with the yield of 0.19 extrapolated to 295 K and atmospheric pressure in the same study.

However, we had not registered that the value of k_1 had been corrected by a factor of two from that given in Orlando and Tyndall (2001), and are very grateful to the referee for alerting us to this. We have therefore repeated the above procedure using the following correct parameters, for use over the atmospheric temperature range: $k_1 = 7.0 \times 10^{11} \exp(-3160/T) \text{ s}^{-1}$; $k_{2a} = 5.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$; $k_{2b} = \alpha \times 5.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$; $k_{2c} = (1-\alpha) \times 5.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Use of an optimised value of $\alpha = 3.2 \exp(-550/T)$ recreates the OH yields reported by Lockhart et al. (2013), 0.38 at 212 K, 0.31 at 250 K and 0.19 at 295 K, and leads to the following relative contributions of the different channels at 295 K in air at atmospheric pressure: 0.23 (1): 0.39 (2a): 0.19 (2b): 0.19 (2c). Because it is based on the reaction framework and parameters reported by Orlando and Tyndall (2001) (and correctly incorporating the adjustment highlighted by the referee) it recreates the [CO]/[CO₂] product ratios reported in that study, and their dependence on temperature and [O₂]; and also those reported much earlier by Niki et al. (1985). We therefore believe the representation provides an acceptable description for application in an atmospheric mechanism. Although it does not recreate the full pressure dependence of the OH yields reported by Lockhart et al. (2013), it does provide an acceptable description of their reported OH formation at pressures close to atmospheric and over the atmospheric temperature range.

Although now a relatively minor channel, the retention of reaction (2b), forming the stabilised peroxy radical HC(O)C(O)O₂, is necessary to account fully for the reported formation of CO₂. Orlando and Tyndall (2001) also inferred that its reaction with NO₂ was necessary as a source of NO₃ in their system, having ruled out other NO₃ sources related to NO₂ photolysis (e.g. the reactions of NO₂ with O or O₃). We therefore also updated the reaction of NO₂ with HC(O)C(O)O₂ to form NO₃, HCO and CO₂ directly, rather than a PAN analogue, as postulated by Orlando and Tyndall (2001).

Comment C2: C3MCOBCO3H and MC3COBCO3H from C4MDIAL are actually the same as C5PACALD1 and C5PACALD2 although on the MCM website they are showed being E- and Z-geometric isomers, respectively. Even if this were the case, they should both undergo fast photolysis as proposed by Peeters et al(2010). However, C3MCOBCO3H and MC3COBCO3H undergo an old and obscure chemistry. I find hard imagining how MC3COBCO3H can yield CH3COCO3H by photolysis. Since C4MDIAL is a common oxidation product of isoprene and aromatics, an updated treatment of C3MCOBCO3H and MC3COBCO3H would result in more OH-recycling for both VOCs. I would like to see the impact of such changes to the modelled HOx concentrations.

Response: We are very grateful to the referee for pointing out these inconsistencies. As indicated, C4MDIAL is mainly produced in the MCM from the degradation chemistry of aromatics, and the representation of its degradation dates back to the original development of the aromatic schemes, as described by Jenkin et al. (2003).

The relevant species, which we think are actually C4COBCO3H and MC3OBCO3H, are formed from the reactions of HO₂ with the acyl peroxy radicals, C3MCOBCO3 and MC3COBCO3, generated (for example) from OH + C4MDIAL. As is generally the case in the MCM, the displayed photolysis products are not primary photo-fragments, but species formed following subsequent reaction sequences that are usually initiated by reaction of each photo-fragment with O₂. By analogy with other aldehydes, the photolysis routes for C4COBCO3H and MC3OBCO3H assumed initial formation of HCO and a vinyl-type radical in each case. The generic chemistry for the vinyl-type radicals following reaction with O₂ (similar to that outlined above in the response to [Comment B2](#))

yields $\text{CH}_3\text{C}(\text{O})\text{C}(\text{O})\text{OOH}$ (and HCO) from MC3ODBCO3H ; and $\text{HC}(\text{O})\text{C}(\text{O})\text{OOH}$ (and CH_3CO) from C4CODBCO3H . The products are not therefore illogical, but result from sequences of reactions for which there were reported precedents in the literature. Such assumptions have always been necessary in detailed mechanism construction, and are applied until improved information (or any information!) is available.

However, we agree with the referee that improved information is now available, and should have been implemented. The commonality of these species with the C5PACALDs was overlooked at least partially because geometric isomers have not previously been routinely distinguished in MCM intermediates. Probably more importantly than updating the products, is that the photolysis rates were based on those for methacrolein, and therefore much too slow. We are in the process of updating this chemistry in MCM v3.3.1, and will make consistent changes to a number of other analogous species (e.g. MALDALCO3H) formed from aromatic degradation.

Although it is very important to implement these corrections, we suspect that the effect on OH recycling will be very small indeed for the isoprene system. The sources of C4MDIAL from isoprene degradation in MCM v3.3.1 are either the further oxidation of minor first generation products such as 3-methyl furan which (as shown in Fig. R3) is represented to be formed in very low yield (< 1 %) under atmospheric conditions; or from minor oxidation routes of more important products (e.g. the OH initiated chemistry of C5HPALD1 and C5HPALD2). The further oxidation of C4MDIAL only partially produces the peroxy radicals, C3MCOBCO3 and MC3COBCO3, which only partially react with HO_2 . The HO_2 reactions are already represented to be significantly (44 %) radical-propagating (with OH-forming channels), such that they only partially form C4CODBCO3H and MC3ODBCO3H. It is therefore likely that implementing the rapid regeneration of radicals (including OH) from their photolysis will have a similar effect to that of the existing propagating channels for the reactions of HO_2 with C3MCOBCO3 and MC3COBCO3. As shown in Fig. 12 of the original manuscript, the total OH recycling from these channels for all acyl peroxy radicals (i.e. including much more abundant species, such as CH_3CO_3 and MACO_3) was calculated to be $\leq 15\%$ of the total (excluding $\text{HO}_2 + \text{NO}$) using MCM v3.3. The contribution from the reactions of HO_2 with C3MCOBCO3 and MC3COBCO3 reactions is actually negligible, amounting to $3\text{--}6 \times 10^{-5}$ of the group total. It is therefore likely that the effect of the corrections on OH recycling will be very small. However, we will also test the impact of the revisions in the revised idealised atmospheric simulations with MCM v3.3.1.

The formation of C4MDIAL (and related products) from aromatic degradation is more significant, with about 35 % being formed from the OH-initiated oxidation of toluene in the MCM (about 12 % being C4MDIAL itself). However, because aromatics are typically emitted in conjunction with NO_x , the reactions of HO_2 with C3MCOBCO3 and MC3COBCO3 (and analogues) will tend to be inhibited under many conditions, and this may limit the formation and impact of C4CODBCO3H and MC3ODBCO3H. It would nonetheless be of interest to test the impact of the updated chemistry, particularly for traditional chamber conditions at the point when NO becomes depleted.

Minor comments

p.9733 l.20-24

This statement is confusing as no direct OH-regeneration from 1,6-H-shift of CISOPA02 and CISOPCO2. Do the authors ascribe the OH generated by 1,4-H-shifts of C536O2 and C537O2 to the 1,6-H-shift of CISOPA02 and CISOPCO2? If this is the case it would be more appropriate to assign this OH generation to 1,4-H-shifts. This way line (1) in Figure 11 is problematic. I suggest the authors to find a way to eliminate this source of confusion.

Response: We agree that this could be clearer. The flux calculation was aiming to illustrate the amount of OH recycling that results from the sequences of chemistry initiated by the 1,6-H-shift of CISOPAO2 and CISOPCO2; but excluding that resulting from C5HPALD photolysis. The total therefore includes that resulting from both the 1,4-H shifts of C536O2 and C537O2, and from the decomposition of C536O and C537O (as shown in Fig. 3). The word “directly” was intended to indicate “not requiring a further initiation reaction”, but we agree that this is confusing. We will find a way to present this more clearly in the revised manuscript.

Technical comments

p.9719 l.19

It should be "Brégonzio-Rozier et al. (2015)" and not "Brégonzio-Rozier et al. (2014)"

Response: Thank you for alerting us to the recent publication of the ACP version of the paper.

References

Atkinson R.: Atmospheric reactions of alkoxy and β -hydroxyalkoxy radicals, *Int. J. Chem. Kinetics*, 29, 99–111, 1997.

Atkinson, R., Aschmann, S. M., Tuazon, E. C., Arey, J. and Zielinska, B.: Formation of 3-methylfuran from the gas-phase reaction of OH radicals with isoprene and the rate constant for its reaction with the OH radical, *Int. J. Chem. Kinet.*, 21, 593-604, 1989.

Aumont, B., Szopa, S., and Madronich, S.: Modelling the evolution of organic carbon during its gas-phase tropospheric oxidation: development of an explicit model based on a self generating approach, *Atmos. Chem. Phys.*, 5, 2497–2517, doi:10.5194/acp-5-2497-2005, 2005.

Baker, J., Arey, J. and Atkinson, R.: Formation and reaction of hydroxycarbonyls from the reaction of OH radicals with 1,3-butadiene and isoprene, *Environ. Sci. Technol.*, 39, 4091-4099, 2005.

Bates, K. H., Crouse, J. D., St. Clair, J. M., Bennett, M. B., Nguyen, T. B., Seinfeld, J. H., Stoltz, B. M. and Wennberg, P. O.: Gas phase production and loss of isoprene epoxydiols, *J. Phys. Chem. A*, 118, 1237-1246, 2014.

Benkelberg, H.-J., Böge, O., Seuwen, R., and Warneck, P.: Product distributions from the OH radical-induced oxidation of but-1-ene, methyl-substituted but-1-enes and isoprene in NO_x-free air, *Phys. Chem. Chem. Phys.*, 2, 4029–4039, 2000.

Brégonzio-Rozier, L., Siekmann, F., Giorio, C., Pangui, E., Morales, S. B., Temime-Roussel, B., Gratien, A., Michoud, V., Ravier, S., Tapparo, A., Monod, A., and Doussin, J.-F.: Gaseous products and Secondary Organic Aerosol formation during long term oxidation of isoprene and methacrolein, *Atmos. Chem. Phys. Discuss.*, 14, 22507-22545, doi:10.5194/acpd-14-22507-2014, 2014.

Calvert, J. G., Atkinson, R., Kerr, J. A., Madronich, S., Moortgat, G. K., Wallington, T. J., and Yarwood, G.: The mechanisms of atmospheric oxidation of alkenes, Oxford University Press, New York, ISBN 0-19-513177-0, 2000.

Carter, W. P. L., and Atkinson, R.: Alkyl nitrate formation from the atmospheric photo-oxidation of alkanes; a revised estimation method. *J. Atmos. Chem.* 8, 165-173, 1989.

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

Crouse, J. D., Knap, H. C., Ørnsø, K. B., Jørgensen, S., Paulot, F., Kjaergaard, H. G. and Wennberg, P. O.: Atmospheric fate of methacrolein. 1. Peroxy radical isomerization following addition of OH and O₂, *J. Phys. Chem. A*, 116, 5756-5762, 2012.

Crouse, J. D., Paulot, F., Kjaergaard, H. G., Wennberg, P. O.: Additions and Corrections to "Peroxy radical isomerization in the oxidation of isoprene", *Phys. Chem. Chem. Phys.* 2011, 13, 13607. <http://www.rsc.org/suppdata/cp/c1/c1cp21330j/addition.htm> 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, CA, Dec. 2014.

Da Silva, G.: Hydroxyl radical regeneration in the photochemical oxidation of glyoxal: kinetics and mechanism of the HC(O)CO + O₂ reaction, *Phys. Chem. Chem. Phys.*, 12, 6698-6705, 2010.

Da Silva, G., Graham, C. and Wang, Z-F.: Unimolecular β-hydroxyperoxy radical decomposition with OH recycling in the photochemical oxidation of isoprene. *Environ. Sci. Technol.*, 44, 250-256, 2010.

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

Francisco-Márquez, M., Alvarez-Idaboy, J. R., Galano, A. and Vivier-Bunge, A.: Theoretical study of the initial reaction between OH and isoprene in tropospheric conditions, *Phys. Chem. Chem. Phys.*, 5, 1392-1399, 2003.

Giacopelli, P., Ford, K., Espada, C. and Shepson, P. B.: Comparison of the measured and simulated isoprene nitrate distributions above a forest canopy, *J. Geophys. Res.*, 110, D01304, doi:10.1029/2004JD005123, 2005.

Jenkin, M. E. and Hayman, G. D.: Kinetics of reactions of primary, secondary and tertiary β-hydroxy peroxy radicals: application to isoprene degradation, *J. Chem. Soc., Faraday Transactions*, 91, 433-446, 1995.

Jenkin, M. E., Saunders, S. M., and Pilling, M. J.: The tropospheric degradation of volatile organic compounds: a protocol for mechanism development. *Atmos. Environ.*, 31, 81-104, 1997.

Jenkin, M. E., Saunders, S. M., Wagner, V., and Pilling, M. J.: Protocol for the development of the Master Chemical Mechanism, MCM v3 (Part B): tropospheric degradation of aromatic volatile organic compounds, *Atmos. Chem. Phys.*, 3, 181-193, doi:10.5194/acp-3-181-2003, 2003.

Karl, M., Dorn, H.-P., Holland, F., Koppmann, R., Poppe, D., Rupp, L., Schaub, A. and Wahner, A.: Product study of the reaction of OH radicals with isoprene in the atmosphere simulation chamber SAPHIR, *J. Atmos. Chem.*, 55, 167-187, 2006.

Kjaergaard, H. G., Knap, H. C., Ornsø, K. B., Jørgensen, S., Crouse, J. D., Paulot, F., and Wennberg, P. O.: Atmospheric fate of methacrolein. 2. Formation of lactone and implications for organic aerosol production, *J. Phys. Chem. A*, 116, 5763-5768, 10.1021/jp210853h, 2012.

Lee, W., Baasandorj, M., Stevens, P. S. and Hites, R. A. : Monitoring OH-initiated oxidation kinetics of isoprene and its products using online mass spectrometry, *Environ. Sci. Technol.*, 39, 1030-1036, 2005.

Lee, L., Teng, A. P., Wennberg, P. O., Crouse, J. D. Cohen, R. C.: On rates and mechanisms of OH and O₃ reactions with isoprene-derived hydroxy nitrates, *J. Phys. Chem. A*, 118 (9), 1622-1637, 2014.

Le Person, A., Solignac, G., Oussar, F., Daële, V., Mellouki, A. W., Winterhalter, R., and Moortgat, G. K.: Gas phase reaction of allyl alcohol (2-propen-1-ol) with OH radicals and ozone, *Phys. Chem. Chem. Phys.*, 11, 7619–7628, 2009.

Lightfoot, P. D., Cox, R. A., Crowley, J. N., Destriau, M., Hayman, G. D., Jenkin, M. E., Moortgat, G. K., and Zabel, F.: Organic peroxy radicals : kinetics, spectroscopy and tropospheric chemistry, *Atmos. Environ.*, 26A, 1805–1964, 1992.

Lin, Y.-H., Zhanga, H., Pye, H. O., Zhanga, Z., Martha, W. J., Parka, S., Arashiroa, M., Cuia, T., Budisulistiorinia, S. H., Sextona, K. G., Vizuetea, W., Xieb, Y., Lueckenb, D. J., Pileticb, I. R., Edneyb, E. O., Bartolottic, L. J., Gold, A., and Surratt, S. D.: Epoxide as a precursor to secondary organic aerosol formation from isoprene photooxidation in the presence of nitrogen oxides, *Environ. Sci. Technol.*, 110, 6718-6723, doi/10.1073/pnas.1221150110, 2013.

Liu, Y. J., Herdinger-Blatt, I., McKinney, K. A., and Martin, S. T.: Production of methyl vinyl ketone and methacrolein via the hydroperoxyl pathway of isoprene oxidation, *Atmos. Chem. Phys.*, 13, 5715-5730, doi:10.5194/acp-13-5715-2013, 2013.

Lockhart, J., Blitz, M., Heard, D., Seakins, P. and Shannon, R.: Kinetic study of the OH + glyoxal reaction: experimental evidence and quantification of direct OH recycling, *J. Phys. Chem. A*, 117, 11027-11037, 2013.

Lockwood, A. L., Shepson, P. B., Fiddler, M. N. and Alaghmand, M.: Isoprene nitrates: preparation, separation, identification, yields, and atmospheric chemistry. *Atmos. Chem. Phys.*, 10, 6169-6178, 2010.

Müller, J.-F., Peeters, J., and Stavrou, T.: Fast photolysis of carbonyl nitrates from isoprene, *Atmos. Chem. Phys.*, 14, 2497-2508, doi:10.5194/acp-14-2497-2014, 2014.

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

Orlando, J. and Tyndall, G. S: The atmospheric chemistry of the HC(O)CO radical, *Int. J. Chem. Kinet.*, 33, 149-156, 2001.

Orlando, J. J. and Tyndall, G. S.: Laboratory studies of organic peroxy radical chemistry: an overview with emphasis on recent issues of atmospheric significance, *Chem. Soc. Rev.*, 41, 6294–6317, doi:10.1039/c2cs35166h, 2012.

Paulot, F., Crouse, J. D., Kjaergaard, Kroll, J. H., Seinfeld, J. H. and Wennberg, P. O.: Isoprene photooxidation: new insights into the production of acids and organic nitrates. *Atmos. Chem. Phys.*, 9(4):1479-1501, 2009.

Paulson, S. E., Flagan, R. C. and Seinfeld, J. H.: Atmospheric photo-oxidation of isoprene: part I. The hydroxyl radical and ground state atomic oxygen reactions. *Int. J. Chem. Kinet.*, 24, 79-101, 1992.

Peeters, J. and Müller, J.-F.: HO_x radical regeneration in isoprene oxidation via peroxy radical isomerisations, II: Experimental evidence and global impact, *Phys. Chem. Chem. Phys.*, 10, 14227-14235, 2010.

Peeters, J. and Nguyen, T. L.: Unusually fast 1,6-H shifts of enolic hydrogens in peroxy radicals: formation of the first-generation C₂ and C₃ carbonyls in the oxidation of isoprene, *J. Phys. Chem. A*, 116, 6134-6141, 2012.

Peeters, J., Nguyen, T. L. and Vereecken, L.: HO_x radical regeneration in the oxidation of isoprene, *Phys. Chem. Chem. Phys.*, 28, 5935-5939, 2009.

Peeters, J., Müller, J.-F., Stavrakou, T. and Nguyen, V. S.: Hydroxyl radical recycling in isoprene oxidation driven by hydrogen bonding and hydrogen tunneling: the upgraded LIM1 mechanism, *J. Phys. Chem. A*, 118 (38), 8625-8643, 2014.

Ruppert, L. and Becker, K.-H.: A product study of the OH radical-initiated oxidation of isoprene: formation of C₅-unsaturated diols. *Atmos. Environ.*, 34, 1529-1542, 2000.

Sprengnether, M., Demerjian, K. L., Donahue, N. M., et al.: Product analysis of the OH oxidation of isoprene and 1,3-butadiene in the presence of NO, *J. Geophys. Res.*, 107, 4269, doi:10.1029/2001JD000716, 2002.

Stavrakou, T., Peeters, J., and Müller, J.-F.: Improved global modelling of HO_x recycling in isoprene oxidation: evaluation against the GABRIEL and INTEX-A aircraft campaign measurements, *Atmos. Chem. Phys.*, 10, 9863-9878, doi:10.5194/acp-10-9863-2010, 2010.

Taraborrelli, D., Lawrence, M. G., Crowley, J. N., Dillon, T. J., Gromov, S., Groß, C. B. M., Vereecken, L. and Lelieveld, J.: Hydroxyl radical buffered by isoprene oxidation over tropical forests, *Nature Geoscience*, 5, 190-193, 2012.

Teng, A. P., Crouse, J. D., Lee, L., St. Clair, J. M., Cohen, R. C., and Wennberg, P. O.: Hydroxy nitrate production in the OH-initiated oxidation of alkenes, *Atmos. Chem. Phys.*, 15, 4297-4316, doi:10.5194/acp-15-4297-2015, 2015.

Yeung, L. Y., Pennino, M. J., Miller, A. M., and Elrod, M. J.: Kinetics and mechanistic studies of the atmospheric oxidation of alkynes, *J. Phys. Chem. A*, 109, 1879-1889, 2005.

Zhao, J, Zhang, R. Y., Fortner, E. C. and North, S. W.: Quantification of hydroxycarbonyls from OH-isoprene reactions, *J. Am. Chem. Soc.*, 126, 2686-2687, 2004.