Authors' responses to referee and discussion comments on: Jenkin et al., Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2019-44.

We are very grateful to the referees for their supportive comments on this work, and for their helpful suggestions for modifications and improvements. Responses to the comments are now provided (the original comments are shown in blue font). We received one additional comment shortly after the discussion closed. This is also reproduced here, along with our response.

A. Comments by Referee 1

General comments:

This manuscript discusses structure-activity relationships for peroxy radicals with its most common co-reactants in atmospheric conditions. The SARs are developed based on a selection of the available literature (mostly experimental data), and aim to provide site-specific rate coefficients and product distributions as appropriate for the reactions studied. The derivation of the SARs is well developed and explained, and the SARs strike a good balance between covering the mechanistic aspects of the target reactions on the one hand, and a pragmatic approach fitting data to a suitable function on the other hand, with good recovery of the training set. The data used as the training set is not an exhaustive literature tabulation. Some experimental data is missing (see also the comment by B. Nozière), and while some theoretical data is used, the potential of combing theoretical and experimental data has not been fully exploited. Overall, however, I feel that reasonable choices were made, giving a good summary of the reactivity trends discernible from the literature data, even if one could have a different view on what data to include in the training set, what weight to assign to each datum (which is not all that obvious especially for theoretical data at lower levels of methodology), or how to parameterize the SAR. What was missing a bit in places is reference to existing SARs and their approaches, but I recognize this paper is focused on presenting a new SAR, and need not be made longer by rigorous review or historic overview.

To put the usability of the SARs to the test, I have applied them in the development of a small mechanism (~100 reactions). The SARs prove to be quite usable even with a simple calculator, though during these efforts I found that adding a few additional subheadings would have made it easier to locate the desired information in the text: e.g. rate coefficients vrs. product distribution; self-reactions versus cross-reactions versus product distributions, etc.

Overall, this paper presents a good overview of the status quaestionis, and presents a set of very valuable SARs. Publication of the paper after minor revisions is recommended.

Response: We are grateful to the referee for these very positive and supportive comments on our work – and also for testing the methods in the development of a small mechanism. It is very gratifying to know that the methods have been found to be practical and usable. We acknowledge the referee's point about sub-headings. We have therefore added "kinetics" and "product branching ratios" subsections to section 2.1 on RO_2 + NO and section 2.5 on RO_2 + HO_2; and "kinetics of self-reactions", and "parameterized representation" subheadings to section 2.6 on RO_2 permutation reactions. Section 2.2 to 2.4 are relatively short, and these have therefore been left without subsections.

Although the tabulations we provide are probably not exhaustive, we feel that they are extensive, and provide good coverage of the hydrocarbon and oxygenated RO_2 *bimolecular* reactions for which there are laboratory experimental data. As stated in Sect. 3, we have not attempted exhaustive coverage of the fast moving topic of *unimolecular* RO_2 radical reactions, which will necessarily need to be revisited in future work (see also response to comments B11-B13).

We have not aimed to list all studies of all bimolecular reactions, but have given an evaluated or preferred rate coefficient for each reaction we tabulate – which we think cover most (if not all) for which there are reported reliable experimental data. In many cases, these are based on evaluations such as those of the *IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation*, and therefore consider data from many studies; as our own evaluations have also done, where possible. We therefore believe the reaction listing is larger than in previous RO_2 reviews, partly because it can

include more recent data. For example, the table below illustrates that data for a larger number of bimolecular reactions of hydrocarbon and oxygenated RO_2 are presented than those appearing in the reviews of Orlando and Tyndall (2012) and Calvert et al. (2015) - noting that those reviews did not claim to be exhaustive, and also consider halogenated peroxy radicals, and reactions with halogenated species (e.g. ClO) that are outside the scope of our study.

Reaction	This work	Orlando and Tyndall (2012)	Calvert et al. (2015)
RO_2 + NO	23	13	14
RO_2 + NO_2 (k_f, k_b)	6, 9	7, 7	5, 6
RO_2 + NO_3	8	5	5
RO_2 + OH	4	-	-
RO_2 + HO_2	23	11	13
RO_2 + RO_2	38	10	10
RO_2 + $R'O_2$	20	3	5

Specific comments:

Comment A1: p. 3, line 22: The generic rate coefficient for RO2 + NO is appropriate for many peroxy radicals, but RO2 derived from aromatics have been reported to have slightly higher rate coefficients. The difference may not warrant a different class, but a short mention might be useful.

Response: We are only aware of one reported experimental rate coefficient for an aromatic-derived RO_2, but would be grateful to be pointed towards other data if available.

The experimental rate coefficient we are aware of is that listed for the 1,3,5-trimethylbenzene-derived RO_2 in Table 1, and is actually slightly lower than the generic value, k_{RO2NO}. This was reported by Elrod (2011) for a mixture of two complex radicals of molecular formula $HOC_9H_{12}[OO]O_2$, although with one isomer likely dominant (as stated in footnote (m) of Table 1). The reported rate coefficient was 7.7×10^{-12} cm^3 molecule^{-1} s^{-1} at 296-298 K, with an estimated error of ± 30 %. This therefore agrees with k_{RO2NO} (9.0×10^{-12} cm^3 molecule^{-1} s^{-1} at 298 K), and was reported by Elrod (2011) to confirm that the use of this same generic value for all aromatic-derived "peroxide bicyclic" RO_2 in the MCM was acceptable.

Comment A2: p. 4, line 17: State explicitly (again) that nCON does not include the peroxy radical oxygen atoms, as an equally logical choice could have been a nCON based on the full molecular stoichiometry, i.e. including all functionalities. It might be useful to have a short reminder in other places as well.

Response: We have further clarified this point as suggested (see also comment B3). The revised text reads as follows in the revised manuscript and SI (new text in red font):

"n_{CON} is the number of carbon, oxygen and nitrogen atoms in the organic group (R) of the peroxy radical (i.e. excluding the peroxy radical oxygen atoms and equivalent to the carbon number in alkyl peroxy radicals), T is the temperature (in K) and [M] is the gas density (in molecule cm^{-3})."

In conjunction with the existing indication that it is equivalent to the carbon number in alkyl peroxy radicals (and must therefore exclude the peroxy radical oxygens), and the n_{CON} = 2 examples, $C_2H_5O_2$ and $HOCH_2O_2$, given in Sect. 2.4 (page 7, line 22 in original manuscript), we believe that readers will understand the definition.

Comment A3: p. 4: The parameterization of the nitrate yield may need to be updated soon following recent work of John Orlando et al (NCAR). No publication is available to my knowledge, but interesting results were presented at conferences; I suggest contacting these authors to see if there is a need for alternative SAR parameters.

Response: We thank the referee for this information. We provide more discussion of the nitrate yield parameterization below in the responses to reviewer comments B3, C1 and D2 and additional comment E1.

Comment A4: p. 7, line 13: formation of CI from CH3O2 + OH: Also state that the small to negligible yield of CI is consistent with theoretical data..

Response: We thank the referee for this information. The relevant sentence has now been amended to read:

"However, no evidence for formation of CH_2O_2 and H_2O has been observed at room temperature, indicating that this product channel is at most minor (< 5%) (Yan et al., 2016; Assaf et al., 2017a; Caravan et al., 2018), this also being consistent with theoretical data (e.g. Müller et al., 2016)."

Comment A5: p. 8, R6c and R6e: R-HO is perhaps better written as R-H=O, unless the authors mean to imply that the H-atom transferred is not necessarily adjacent to the peroxy radical group.

Response: The referee is correct that the transferred H-atom is adjacent to the peroxy radical group. The product is therefore now represented as $R_{-H}=O$ (or $R'_{-H}=O$) at all relevant points in the manuscript.

Comment A6: p. 10: readability might be improved if using a notation for kRO2RO2 that indicates whether an expression pertains to self-reactions vrs. cross-reactions. Additional subheadings might be useful to make finding specific topics easier when applying the SAR (reference self reactions, self reactions, cross reactions, branching ratios,...).

Response: We agree with the referee that this (quite long) section was quite difficult to navigate through, and have added subheadings for "kinetics of self-reactions" and "parameterized representation". To clarify, the rate coefficient expressions either refer to the "self-reactions" (i.e. Eqs (14)-(17)), or to the "parameterized representation of the permutation reaction reactions" (i.e. Eqs (21)-(25)) and now appear in the "kinetics of self-reactions" and "parameterized representation" subsections, respectively. The k_{RO2RO2} parameters always refer to self-reactions, and the shorter parameters, k_{AP} and k_{RO2}, refer to the pseudo-unimolecular parameterized representation. We agree that this is clearer with the new section structure.

Comment A7: p. 11: line 29: "... if the peroxy radical contains more than one benzyl group". A benzyl group is C6H5-C.H2, and there can be only one. The authors probably mean multiple beta-phenyl groups?

Response: Within a strict definition, we acknowledge that the referee is correct. In fact, we are using benzyl even more generically in this discussion to mean a β-aryl group (i.e. including β-phenyl groups and substituted β-phenyl groups). We have now therefore changed "benzyl" to "β-aryl" at the relevant points in the manuscript. Accordingly, we have also changed generic uses of the term "phenyl" to "aryl".

Using the referee's reasoning, it is probably also strictly incorrect to use the term "allyl" generically, as this refers specifically to $CH_2CHC.H_2$ – although the term "allyl" seems to be used very widely as a generic term for all alk-2-enyl groups. We have now therefore also changed "allyl" to the more generic term "allylic" at the relevant points in the manuscript.

Comment A8: p. 11, line 29: the formula for calculating alpha and beta needs an equation number to allow unambiguous references in implementations.

Response: This has been rectified in the revised manuscript.

Comment A9: p. 12: line 7: "This is regarded as a logical choice, because CH3O2 is the most abundant organic peroxy radical in the atmosphere". An explicit or semi-explicit mechanism as seems to be the target here is not used all that often for global modeling or even regional modeling as they tend to be too large. Without having access to any reliable statistical data, I would guess that e.g. the MCM

Response: The referee raises some interesting points. Based on previous applications of the MCM and GECKO-A, the mechanisms to which the methods will be applied are likely to be very varied. In the paper we present (i) methods for estimating self- and cross-reaction rate coefficients (i.e. Eqs. (17) and (20)) that could be used in a fully explicit representation; (ii) a parameterized method involving 9 reactant peroxy radical classes that can be used in a highly explicit mechanism; and (iii) a parameterized method based on a single reactant peroxy radical class, which can be used to limit the number of permutation reactions further, as required. We therefore cover a wide variety of possible applications. The choice to present the simpler parameterization in the main paper was primarily to limit the length of an already quite long section, with this logically expanded to the related 9 class parameterization in the SI. This was not intended to imply that the single class parameterization is our recommended method. That we have presented the 9 class parameterization confirms that we have covered the referee's preferred approach (as stated in the final sentence of comment A9), along with information that hopefully serves the needs of others.

The single class parameterization has traditionally been used in the MCM as one simplification measure. The MCM has been applied in regional models (e.g. Li et al., 2015), and is frequently used as a reference benchmark in reduced mechanism development. We would therefore like to provide further explanation here of why CH_3O_2 is a logical choice for defining the parameterized rate coefficients for reactions of non-acyl peroxy radicals with the single-class RO_2 pool. CH_3O_2 is invariably simulated to be the most abundant peroxy radical in the atmosphere, present at sufficient concentration to make it a major reaction partner – and usually the major reaction partner. Even in the isoprene dominated tropical boundary layer simulations of Jenkin et al. (2015), it accounted for between 35 % and 40 % of the peroxy radical population across the wide NO_x range considered (about 30 ppt to 8 ppb). As stated in the current paper, it is also in the middle of the peroxy radical self-reaction reactivity range. For example, its self-reaction rate coefficient (3.5×10^{-13}) is intermediate between those reported for the two most abundant OH + isoprene-derived peroxy radicals (0.69 and 57×10^{-13}; geometric mean 6.3×10^{-13}) and between those calculated here for large secondary and tertiary β-hydroxy peroxy radicals (0.079 and 15×10^{-13}; geometric mean 1.1×10^{-13}), as formed, for example, from reaction of OH with a number of monoterpenes and sesquiterpenes (e.g. α-pinene, limonene, β-caryophyllene).

However, we agree with the referee that the MCM has been widely used to simulate a variety of chamber systems, and that the alternative 9 class parameterization or an explicit representation might be more appropriate in some cases. When tractable, MCM authors have always verbally recommended using an explicit representation of peroxy radical self- and cross-reactions, although this recommendation has not been stated on the website. Of course, the current paper is not discussing current or past versions of the MCM, it is aimed at providing the basis for the automated generation of the next generation of mechanisms, with the potential for providing optional approaches. As indicated above, the methods presented therefore cover a wide range of possible applications where a representation of peroxy radical permutation reactions might be required.

Comment A10: Figures: While I recognize that adding uncertainty intervals on all the underlying data would make the figures visually cluttered, it could be useful to indicate somewhere in the caption what the typical uncertainty or scatter is on the data points underlying the fitting parameters.

Response: We investigated including error bars on the plots, and can confirm that this does generally make them very cluttered and unclear. However, we agree that some indication of scatter would be helpful, particularly on plots with a log scale. In view of the referee's comment (see also response to comment B8), we have included lines showing factor of three increase and decrease ranges in Fig. 4; and note that Fig. 5 already includes a line illustrating a factor of two change in the rate coefficient.

Comment A11: SI, page 7, "The reaction of OH with ROOOH is expected to occur significantly by initial addition to the OOOH group". There are no free orbitals to accommodate an addition of OH, only abstraction, complexation, and substitution. I propose "... by initial attack on the OOOH group".

Response: We thank the referee for pointing out this error, which has been corrected as suggested in the revised SI.

B. Comments by Paul O. Wennberg (Referee)

Opening comment:

In this study, Jenkin and colleagues describe the formulation of 'rules' for the rate coefficients and product yields for reactions of organic peroxy radicals for use in mechanism construction. This manuscript documents how these rules are created and is not intended as a full review of the state-of-knowledge of such reactions. As a result of this scope (which is understandable and indeed necessary), at times this reviewer wishes for more detailed discussion of the choices made and critical review of the background literature. Clearly, however, this is not necessary within the context of the goals of this paper. That said, below I highlight a few areas where I believe the authors might go further in justifying and improving their description of the RO2 chemistry. It would also be helpful if the authors address at the onset what is meant that these 'rules' are meant to "guide" the mechanism development. Please explain, for example, how, within the new MCM / GECKO framework, the authors intend to reconcile differences between specific reactions where experimental data exist and the rules/SAR based estimates (e.g. will the latter take precedent or the former in setting the rates / products?).

Response: We thank the referee for these positive comments on our work, and for the suggestions for additions and improvements.

The referee asks for additional information on how the methods are applied, and we are pleased to provide an overview here. The main aim of this work is to document a set of estimation methods (SARs and generic rate coefficients) which can be used define the chemistry of peroxy radicals in mechanism development. It therefore has broadly the same aim as previous published SAR studies, and follows on from our preceding papers covering OH + VOC reactions (e.g. Jenkin et al., 2018). It very much fits into the strategy outlined by Vereecken et al. (2018) (cited in our Introduction) to help promote the sustainable development of chemically detailed mechanisms that reflect current kinetic and mechanistic knowledge.

The methods, or rules, presented in our paper are intended to be formulated to allow practical use in automated mechanism generators. They therefore contribute to a *detailed chemical protocol* that allows a generator to produce fully explicit chemical mechanisms, containing all reactions of all intermediates. This is the first step in the process.

In practice, such mechanisms are of course too large to be usable (e.g. see Aumont et al, 2005), and a *reduction protocol* also needs to be defined. This is a further set of rules that allows the mechanisms to be trimmed or simplified (e.g. by omitting minor reaction channels beneath a threshold contribution). These methods are under revision, and may in any case vary depending on the intended application of the mechanism being generated. These methods will therefore be reported in future mechanism generation/application papers, and are generally not reported here. The only exceptions to this are the parameterization options for the peroxy radical permutation reactions, which will likely be required in most applications.

The vast majority of the reactions in a generated mechanism are unstudied (e.g. MCM v3.3.1 contains about 1200 RO_2 radicals which all need to react). However, for the small subset of reactions for which there are measured data, the preferred data set is used to overwrite the relevant estimated parameters (i.e. a reliable experimentally-determined parameter does indeed take precedence over an estimated parameter).

Comment B1: Specific comments (Page#.Line#):

2.22 In general where the competition is with NO, I'd suggest using 'NO' rather than 'NOx'..

Response: Although a very minor point indeed, we generally agree with the referee. At this point, however, the preceding paragraph has summarized the reactions of RO_2 radicals with NO and NO_2 (i.e. NO_x) and the related species NO_3. The discussion is moving on to reactions with other species, so we feel the term "NO_x" is appropriate here.

Comment B2: 2.29 HOMs: Include reference to Bianchi, 2019 - https://pubs.acs.org/doi/10.1021/acs.chemrev.8b00395

Response: Thank you for alerting us to this very recent review paper, which is cited in the revised manuscript as suggested.

Comment B3: 4.13 I believe that Teng was the first to point out that for multifunctional compounds, the nitrate branching ratios should (and do) scale more closely with heavy atoms than just carbon. Perhaps "updated by Arey et al. (2001) and Teng et al. (2015)"? In your definition of n(NCO), does the peroxy radical moiety count towards the 'O'? I'd suggest being explicit.

Response: Thank you for this suggestion. The Teng et al. (2015) work is now cited at this point in the revised manuscript (see also the responses to the related referee comments C1 and D2 and additional comment E1). As indicated above in the response to referee comment A2, we have further clarified the definition of n_{CON} in the revised manuscript and SI.

Comment B4: 7.16 Should note that Caravan (2018) found a somewhat larger R5b/R5 (to methanol) at higher pressure.

Response: Caravan et al. (2018) report a methanol yield 6-9 %, based on MPIMS measurements at both 30 Torr and 740 Torr. The additional formation at the longer time scales in their chamber experiments was reported to have a contribution from heterogeneous conversion of the low yield of CH_3OOOH formed. They applied a value of 7 % in their global model calculations (based on their MPIMS measurement of a 6-9 % yield), with this agreeing with theory. We therefore decided not to overcomplicate the text, as yields for several different channels are being discussed.

Comment B5: 7.17&7.22Worth noting that Muller (2016) calculate that R5c/R5 is ~ .1 for CH3OO and Caravan (2018) suggest that they do see some CH3OOOH from this reaction.

Response: We have now included this point, although we have instead cited the result of the Assaf et al. (2018) calculation for consistency with our approach to formation of larger ROOOH products in the subsequent paragraph. The added text reads:

"It is noted that Caravan et al. (2018) also reported evidence for minor CH_3OOOH formation at atmospheric pressure, via channel (R5c), although this has been calculated to be formed in very low yield (1.7 %) by Assaf et al. (2018)."

Comment B6: 8.8 Given that your fit to kHO2RO2 vs nCON is identical to that shown in Wennberg et al., 2018, figure 2, I guess that nCON does not include the peroxy moiety? We didn't weight our fit by the stated uncertainty - perhaps that should be done? Also, although we didn't consider this in our isoprene review, I expect that the T-dependence will depend on nCON at some level (presumably less strong for large nCON). For large n and low T, for example, the current parameterized rate will exceed that for kAPHO2 – this seems unreasonable.

Response: As indicated above in the response to referee comments A2 and B3, we have further clarified the definition of n_{CON} in the revised manuscript and SI.

Fig. 2 does graph the same quantities as the figure in Wennberg et al. (2018), although it also includes data for some additional peroxy radical classes. We had not realised the fitted parameters (based on alkyl peroxy and β-hydroxy peroxy radical data) were essentially identical to Wennberg et al. (2018), as this analysis was carried out in 2016 and is only now being presented in a publication. It is a logical extension to our previous use of this type of function for the $RO_2 + HO_2$ reaction (e.g. Jenkin et al., 1997); with the change from carbon number to n_{CON} being consistent with our approach for representing the size dependence of the yield of thermalized α-hydroxy peroxy radicals from the reactions of α-hydroxyalkyl radicals with O_2. That was published in an earlier paper in this series (Jenkin et al., 2018). We also considered using the mass of the organic group, which works equally well.

Weighting the analysis, based on reported uncertainty, actually has little effect. This is because most of the points are quite close to the curve. A significant change would require one of those farthest from the line to be much more precisely determined than the rest – which is not the case.

As we indicated at the relevant point in the manuscript, the temperature dependence is typical of that reported for > C_2 alkyl and β-hydroxy RO_2 radicals (see Fig. R1, below) and remains unchanged from that applied previously by Saunders et al. (2003) – as also adopted by Wennberg et al. (2018). On the basis of the (albeit limited) data, it would seem difficult to justify making the temperature dependence weaker as n_{CON} increases. Additional temperature-dependent data for large peroxy radicals are clearly required to confirm or modify this assumption.

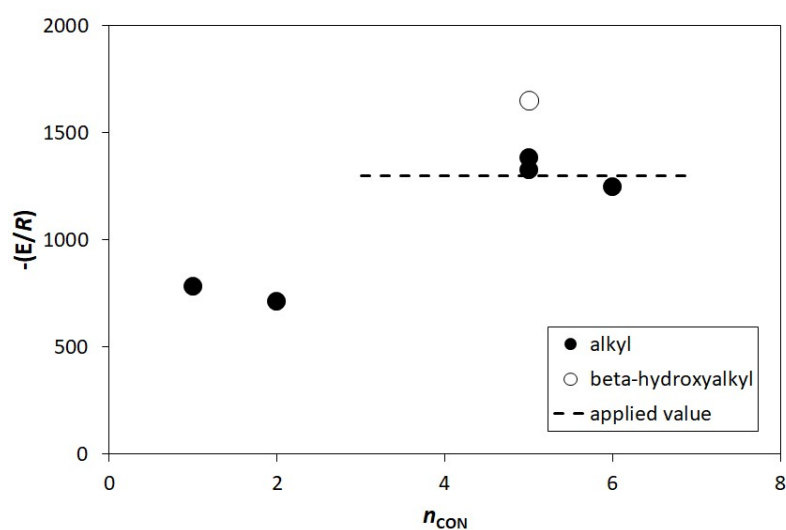Fig. R1 Temperature coefficients for reactions of alkyl and β-hydroxyalkyl RO_2 radicals with HO_2 as a function of n_{CON}.

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The referee is correct that k_{RO2HO2} will exceed k_{APHO2} if the temperature is reduced enough. This is because of the weaker temperature dependence applied to k_{APHO2}, this being based on the value for $CH_3C(O)O_2 + HO_2$. Although data are scarce, the only other rate coefficient for an acyl peroxy radical ($C_6H_5C(O)O_2$) also has a reported weak temperature coefficient (see Table 7) - again, additional temperature-dependent data for large peroxy radicals are required. Based on the coefficients we originally reported for the high n_{CON} limit, the cross-over occurred at about 230 K, with k_{RO2HO2} and k_{APHO2} still within a factor of 1.4 at 210 K.

Since we submitted the paper, Hui et al. (2019) have published a new temperature-dependent kinetics and branching ratio study for $CH_3C(O)O_2 + HO_2$ (extending down to below 230 K), the first to report the temperature-dependence of the OH-forming channel. Although their results support our

use of a reduced temperature dependence for the rate coefficient (compared with earlier $CH_3C(O)O_2$ + HO_2 data), their reported value, E/R = -(720 ± 170) K, is slightly stronger than the value of -580 K that we used. We have therefore revised our parameterization to take account of this – and this slightly reduces the high n_{CON} cross-over temperature to about 225 K, with k_{RO2HO2} and k_{APHO2} still within a factor of 1.2 at 210 K. Given that these temperatures are well outside the studied range of most RO_2 + HO_2 reactions, we feel this is acceptable.

The resultant updated information on the treatment of acyl peroxy + HO_2 reactions in the revised manuscript is now summarized:

(i) The revised kinetics entry for $CH_3C(O)O_2$ in Table 7 is as follows:

Peroxy radical	A	E/R	$k_{298\ K}$	Comment
	(10^{-13} cm^3 molecule^{-1} s^{-1})	(K)	(10^{-12} cm^3 molecule^{-1} s^{-1})	
Acyl $CH_3C(O)O_2$	17.9	-720	20.0	(m)

^{m} $k_{298\ K}$ based on Groß et al. (2014), Winiberg et al. (2016) and Hui et al. (2019). E/R based on Hui et al. (2019) (see Sect. S4);

Regarding product branching ratios, footnote (b) in Table 8 has also been updated to read:

"Based on studies of $CH_3C(O)O_2$ (Niki et al., 1985; Horie and Moortgat, 1992; Hasson et al., 2004; Jenkin et al., 2007; Dillon and Crowley, 2008; Groß et al., 2014; Winiberg et al., 2016; Hui et al., 2019); see Sect. S4. Hasson et al. (2012) also reported broadly comparable branching ratios for $C_2H_5C(O)O_2$ and $C_2H_5C(O)O_2$;"

(ii) Eq. (10) and preceding text in (new) sub-section 2.5.1 now reads:

"Based on the limited data for acyl peroxy radicals (see Fig. 2 and Table 7), and specifically that for $CH_3C(O)O_2$, the 298 K rate coefficients are assigned values that are almost a factor of two greater than those defined by Eq. (9). The temperature dependences reported for acyl peroxy radicals appear to be weaker than those for similar sized radicals in other classes, and the temperature coefficient is again based on that recommended for $CH_3C(O)O_2$. The following expression is therefore assigned to acyl peroxy radicals:

$$k_{APHO2} = 3.6 \times 10^{-12}\ exp(720/T)\ [1\text{-}exp(\text{-}0.23n_{CON})]\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1} \tag{10}"$$

Fig. 2 has also been slightly modified as a result.

(iii) The description of the temperature dependence of the channel branching ratios/rate coefficients in (new) sub-section 2.5.2 now reads (new or adjusted text in red font):

"….This class of reaction (in particular the reaction of HO_2 with $CH_3C(O)O_2$) has received the most attention, and is also a class for which radical propagation is reported to be particularly important at temperatures near 298 K. As shown in Table 8, channels (R6a), (R6b) and (R6d) are reported to contribute. The temperature dependence of k_{6d}/k is based on the recent study of the $CH_3C(O)O_2$ + HO_2 reaction reported by Hui et al. (2019). The contributions and temperature dependences of k_{6a}/k and k_{6b}/k also take account of the wider database for the same reaction, in particular the experimental characterization of k_{6a}/k_{6b} reported by Horie and Moortgat (1992). This procedure (described in detail in Sect. S4) results in the following fitted Arrhenius expressions for the individual channel rate coefficients:

$$k_{6a\ APHO2} = 3.11 \times 10^{-12}\ exp(473/T)\ [1\text{-}exp(\text{-}0.23n_{CON})] \tag{11}$$

$$k_{6b\ APHO2} = 9.14 \times 10^{-15}\ exp(1900/T)\ [1\text{-}exp(\text{-}0.23n_{CON})] \tag{12}$$

$$k_{6d\ APHO2} = 9.68 \times 10^{-12}\ exp(225/T)\ [1\text{-}exp(\text{-}0.23n_{CON})] \tag{13}$$

The corresponding temperature dependences of the channel rate coefficients, derived from the $CH_3C(O)O_2$ data, are thus applied to all (non-aryl) acyl peroxy radicals. The variation of the branching ratios and channel rate coefficients are illustrated for the $CH_3C(O)O_2$ + HO_2 reaction in Figs. S2 and S3, for the 230-300 K temperature range. Summation of the channel rate coefficients given in Eqs. (11)-(13) reproduces the values of k_{APHO2} calculated for the overall reaction using Eq. (10) to within 5 % over this temperature range (see Sect. S4 for further details)."

Comment B7: 8.24 "is taken to be the default where no information is available". This is the type of comment that I do not know how to interpret. In this context, does that mean for any RO2 + HO2 not described in Table 8?

Response: The referee has interpreted the statement correctly. The answer to this question is actually given in footnote (a) of Table 8, where it states that formation of ROOH and O_2 is "…also used as a default in all cases other than those covered by comments (b)-(i)." We suspect most readers wanting to apply the information would examine Table 8 where the guidance is provided, and have therefore now added an additional reference to that table in the sentence quoted by the referee. We believe that Table 8 covers those systems for which evidence for the other product channels has been established. Unlike reviews of atmospheric chemistry, mechanism development protocols necessarily need to provide guidance on how to proceed when information is lacking.

Comment B8: 9.17 (section 2.6). Thank you for engaging with Barbara Noziere's comment on this manuscript. I concur with her that the reported uncertainties in many RO2 + RO2 studies are underestimated given the (often) under-constrained observations of only bulk RO2 abundances. Thus, using reported uncertainty as a screen for which studies to include in formulating the SAR needs to be done critically. While the data shown in Figs. 4 and 5 gives some confidence in the resulting parameterizations, the log-log presentation hides the disagreement somewhat. Perhaps worth including a residual (fit-measure/measure) as a second panel.

Response: The present authors include members of data evaluation panels, and therefore fully concur with the referee's point about critical evaluation. The referee is correct that the many kinetics studies using UV absorption detection were complicated by overlap of the peroxy radical absorption spectra, and therefore required careful interpretation and assessment. However, they were nonetheless direct measurements based on observation of the time-dependence of (initially) relatively simple chemical systems. Reported uncertainties may indeed be too low in some studies (particularly for complex systems in which sequential formation of a number of peroxy radicals occurs), but many studies base their uncertainties on reasonable sensitivity analyses and are therefore more reliable estimates. In practice, the majority of the reported kinetics studies of peroxy radical self-reactions, cross-reactions and reactions with HO_2 are based on this type of measurement, which collectively form a substantial and invaluable data base.

It is, of course, important and desirable that new and complementary methods are applied to confirm or challenge rate coefficients reported in those previous studies. Ideally, these should have the advantage of speciated detection of the reacting peroxy radicals, but without losing the advantages of direct time resolved observations of (initially) relatively simple chemical systems. As a result of our discussions with Barabara Nozière, we have factored in some of the Nozière and Hanson (2017) data into our tabulations. Their work has the advantage of speciated detection of peroxy radicals of different mass, although the method of extraction of kinetic data is less direct than in the UV absorption studies (i.e. based on perturbations to "steady state" concentrations at the exit of a flow tube). However, following critical evaluation, we have not taken account of their data for *t*-butyl peroxy radical kinetics, which seem to be subject to a number of significant complications and interferences – most notably the more significant production of the isomeric *i*-butyl peroxy radical in their system (see discussion comment SC3: Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2019-44-SC3, 2019). Despite these complications, their extracted cross-reaction rate coefficients (nominally) for *t*-butyl peroxy radicals are all apparently close to the geometric mean of the self-reaction rate coefficients (i.e. the expected target value without complications), which we do not fully understand.

We thank the referee for the suggestion of including panels presenting the (calc-obs)/obs deviation, which we have considered carefully. However, having prepared such panels, it was apparent that they only repeated similar information to that which is already clear from the existing figures. This is because the vertical deviation of the points from the line on a log scale is a direct measure of the factor by which the values differ. In Fig. 4, we have instead included lines showing the factor of three increase and decrease ranges, within which all but one of the points fall (with most being much

closer). We think this is an acceptable alternative. In Fig. 5, a factor of two increase line is already included. No additional lines are added to avoid making the figure too cluttered.

Comment B9: 13.20 Add Ng et al. to list of 'ROOR' studies - https://www.atmos-chemphys.net/8/4117/2008/

Response: We thank the referee for this suggestion. This reference has now been included at the relevant point.

Comment B10: 13.16 Given all the recent results (e.g. those listed in 13.20), I don't see a reason not to recommend (generically) a few percent branching yield for R'OOR formation. I suspect that this is more correct than assuming 0% as is currently done.

Response: We agree that there is increasing evidence for the formation of ROOR/R'OOR, and that it is possible to do what the referee suggests in an explicit representation of the chemistry. The issue we are discussing here is the practical difficulty in representing this channel in the pseudo-unimolecular parameterization of the permutation reactions involving reaction with a pool (or pools) of peroxy radicals. This is because only the RO- substructure deriving from the reacting RO_2 can be represented in the product (i.e. the -OR' substructure relates to the variable distribution of peroxy radicals in the pool(s) and cannot be incorporated into the product). We put forward the basis of a possible (compromise) approach, but feel that much more information is required before this can be defined more fully, and we are keeping this under review. In view of the referee's comment, we have made it clearer that we are discussing the parameterization, both through inclusion of subsection headings (suggested by Reviewer A, General comments); and though a number of minor changes to the subsequent paragraph, which now reads as follows (new or adjusted text in red font):

"Although not currently included in the parameterized representation, channel (R9d) is listed to acknowledge the potential formation of peroxide products (i.e. reactions (R7c) and (R8d)). Although these channels have generally been reported to be minor for small peroxy radicals (e.g. Lightfoot et al., 1992; Orlando and Tyndall, 2012), recent studies suggest that they may be more significant for larger peroxy radicals containing oxygenated substituents, and they have been reported to play a role in the formation of low volatility products in a number of studies (Ziemann, 2002; Ng et al., 2008; Ehn et al., 2014; Jokinen et al., 2014; Mentel et al., 2015; Rissanen et al., 2015; Berndt et al., 2015; 2018a; 2018b; Zhang et al., 2015; McFiggans et al., 2019). These reactions may therefore play a potentially important role in particle formation and growth in the atmosphere. The product denoted "RO$_{(peroxide)}$" in reaction (R9d) notionally represents the monomeric contribution the given peroxy radical makes to the total formation of (dimeric) peroxide products. However, it is not an independent species for which subsequent gas phase chemistry can be rigorously defined, such that reaction (R9d) cannot be universally represented within the parameterization. In principle, it could be included for the permutation reactions of a subset of larger peroxy radicals, with the RO$_{(peroxide)}$ product assumed to transfer completely to the condensed phase (i.e. not participating in gas phase reactions). However, there is currently insufficient information on the structural dependence of the contributions of channels (R7c) or (R8d) to the overall self- and cross-reactions to allow the branching ratio of channel (R9d) to be defined reliably. Further systematic studies of these channel contributions are therefore required as a function of peroxy radical size and functional group content."

Comment B11: 14.1 Recognizing that this is a fast-moving area of research, Section 3 still seems a bit cursory and could be advanced using some recent literature as guidance. I believe that this is worth the time as there is now wide recognition that H-shift and endocylization reactions are important in many systems.

To more accurately capture this chemistry, the parameterization used could be improved using new observations and theoretical calculations (the section is currently based largely on older literature). Here are some of the recent literature I am aware of that could be used to broaden and deepen the recommendations:

Mohamed, 2018: https://pubs.acs.org/doi/pdfplus/10.1021/acs.jpca.7b11955

Otkjaer, 2018: https://pubs.acs.org/doi/abs/10.1021/acs.jpca.8b06223

Praske, 2017: https://www.pnas.org/content/115/1/64

Praske, 2018: https://pubs.acs.org/doi/10.1021/acs.jpca.8b09745

Bianchi, 2019: https://pubs.acs.org/doi/10.1021/acs.chemrev.8b00395

Xu, 2019: https://pubs.acs.org/doi/10.1021/acs.jpca.8b11726

Moller, 2019: https://pubs.acs.org/doi/10.1021/acs.jpca.8b10432

Comment B12: 14.22 Xu, 2019 offers new experimental and theoretical calculations for peroxy radical unimolecular chemistry following addition of OH and O2 to alpha and beta pinene that could be added to Table 14.

Comment B13: 14.28 Otkjaer, 2018 offers high-level calculations of ring-size and constituent dependence of the H-shift chemistry for a number of organic substrates that should provide guidance for a first estimate for the rates of these reactions for consideration in the auto-generated mechanism.

Response to comments B11-B13: We are very grateful to the referee for listing these references. These illustrate very well that this is a very fast moving area of research, and would seem to vindicate our decision not to attempt an exhaustive treatment at this stage. Although we might have included the earlier studies in the above list, we note that four of the papers have been published since 14th December 2018, two of them since our paper was submitted (18th January 2019), with one published less than two weeks before the referee posted his review. Because studies will no doubt continue to emerge rapidly over the coming months, we are fully aware that we will need to revisit the topic of unimolecular RO$_2$ reactions before we can attempt to define a set of SARs for automated mechanism generation, as we stated.

We have been unable to assimilate all this information, and work it up into a set of SAR methods, on the time scale of this discussion response. We have therefore edited the section to include the above references. We have re-emphasized at a number of points that the topic continues to be considered in ongoing work, and that a more complete treatment will be developed. The relevant changes to the paper are as follows:

(i) The introductory text in Sect. 1 has been changed to read (new or moved text in red font):

"In this paper, published data on the kinetics and branching ratios for the above bimolecular reactions of hydrocarbon and oxygenated RO$_2$ radicals are reviewed and discussed. Preliminary information is also presented for selected unimolecular isomerization reactions, which continue to be considered in ongoing work. The information on bimolecular reactions is used to define and document a set of rules and structure-activity relationship (SAR) methods (a chemical protocol)…".

(ii) The references listed by the referee are now all cited in the introductory text in Sect. 3.

(iii) Because it does not only consider ring-closure reactions, the information from Xu et al. (2019) has not been included in Table 14. However, the following text has been added at the relevant point in Sect. 3.1:

"It is noted that Xu et al. (2019) have also very recently reported information for a series of isomerization reactions (including ring-closure reactions) for the α- and β-pinene systems, which are being considered in ongoing work."

The captions to both Tables 14 and 15 have been adjusted to indicate that the rate coefficients are currently representative rather than assigned. Although some may become the assigned rate coefficients in the finalized method, this provides the flexibility to update methods.

(iv) In the final paragraph of Sect. 3.2, the text about the need for information on 1,n H-shift reactions has been amended to read (new or adjusted text in red font):

"….requires systematic information on the rates of a series of 1,n H-shift reactions from C-H and O-H bonds in different environments. In this respect, it is noted that the systematic influence of a series of neighbouring functional groups and transition state sizes have been considered in theoretical studies of a number of model systems (e.g. Crounse et al., 2013; Jørgensen et al., 2016; Praske et al., 2017; Otkjaer et al., 2018). Such studies provide the basis for defining systematic structure-activity methods for a wide range of RO$_2$ radicals and their potential isomerization reactions, and are being considered in ongoing work."

We hope the above changes are acceptable. We did consider removing completely (i.e. deferring) the detailed information on unimolecular reactions of RO_2 radicals (Sect. 3), and retitling the paper to specify "bimolecular reactions". Although we recognize that Sect. 3 is preliminary, we feel it is nonetheless important that it is included. This is partly because some of the information it contains (e.g. the rate coefficients for the 1,4 hydroxyl H-shift reactions for stabilized α-hydroxy peroxy radicals in Table 15) dovetails with information presented in the preceding paper on OH + aliphatic VOCs. In addition, it is important to emphasize that this is an important and fast moving topic area, which would be less well achieved by omitting the section completely.

Comment B14: 14.28 Table 15. Should make clear what are calculated and experimental determinations. Also, k298K of alpha-formyl peroxy radicals the rate should be 0.57 s-1 (typo).

Response: Thank you very much for spotting this error, which has been corrected.

Comment B15: 15.22 (and in SI) Assuming that the new mechanism will retain at least to the two radical pools produced following OH addition to isoprene, I do not understand why the 1,6 H-shift rates are not treated separately given there is significant evidence (Crounse, Teng) that a much larger fraction of the chemistry following addition at C4 will undergo this H-shift. Because the H-shift rates (not rate coefficients) for the C1 and C4 addition differ by an order of magnitude, use of the geometric mean will yield significant errors. Thus, I suggest it would be prudent to follow the recipe (if not the rates) described in Wennberg et al., 2018; Teng et al., 2018.

Response: We confirm that the method is exactly as the referee suggests for the isoprene-specific species. We think this is clearly stated at a number of points. The text starting from page 15 line 22 (discussing the generic rate coefficients in Table 15) reads as shown below. The final sentence indicates that the species-specific rate coefficients (rather than generic rate coefficient) are applied to the isoprene-derived species themselves:

"The rate coefficient assigned to the 1,6 hydroxyalkyl H-shift reaction is the geometric mean of rate coefficients applied to (Z)-$CH_2(OH)C(CH_3)$=$CHCH_2O_2$ (CISOPAO2) and (Z)-$CH_2(OH)CH$=$C(CH_3)CH_2O_2$ (CISOPCO2) in MCM v3.3.1. As discussed by Jenkin et al. (2015), those rate coefficients are derived from the LIM1 calculations of Peeters et al. (2014), but with some scaling to recreate the observations of Crounse et al. (2011; 2014). The generic rate coefficient is applied generally to unsaturated δ-hydroxy peroxy radicals containing the sub-structure shown, but with the exceptions of CISOPAO2 and CISOPCO2 themselves, for which the species-specific rate coefficients are applied (see Sect. S6 and Table S5)."

Similarly, the relevant footnote (g) in Table 15 reads:

".... Applied generally to unsaturated δ-hydroxy peroxy radicals containing the sub-structure shown, except for CISOPAO2 and CISOPCO2 themselves for which the species-specific rate coefficients are applied (see Table S5)."

Finally, Table S5 gives the species specific rate coefficients for the isoprene-derived species from MCM v3.3.1, with those from Wennberg et al. (2018) also provided in the footnotes to Table S5 and discussed in Sect. S5.

Comment B16: 16.1-9 The literature cited above goes some way towards meeting the recommendations presented in this paragraph. I'd recommend considering them in the 'rules' developed in this work.

Response: We thank the referee again for alerting us to the recent work, which will indeed help in the formulation of methods in ongoing work. We hope that the way we have dealt with this issue in the current paper is appropriate and acceptable.

C. Comments by Luc Vereecken (Referee)

Comment C1: Prof. Wennberg notes that "Teng was the first to point out that for multifunctional compounds, the nitrate branching ratios should (and do) scale more closely with heavy atoms than just carbon."

Historically, that is not quite accurate, as this has been discussed as far back as the turn of the century, and several models incorporated nitrate yields that are based on the number of heavy atoms, or even estimates that try to account for rigidity and other factors affecting quantum state density and hence lifetime/pressure dependence. Much of this was based on theoretical state density and partition function calculations, and this data was exchanged e.g. during Eurotrac meeting around the years 2000.

Mechanistically, it is clear that the pressure dependence is due to collisional stabilisation which, given that the energetics are not all that different between different RO2+NO reactions, is thus directly linked to the state density of the peroxy nitrite intermediate. This is mostly governed by the low-frequency modes, i.e. the number of modes generated by the molecular skeleton containing the heavy atoms, whereas the H-atoms only contribute by providing a bit of mass, a high-frequency modes that are barely excited at room temperature and thus don't contribute significantly to the state density. These theoretical state density calculations were used by e.g. Jozef Peeters to construct more complex models that weighted for e.g. double bonds and rings that do not contribute to high-density internal rotations and are thus not as effective as single-bonded chains in increasing the lifetime and hence nitrate yields.

In our work, such models were used as far back as 2001 (a-pinene oxidation, Peeters et al.), and as recent as 2012 (b-pinene oxidation, Vereecken and Peeters) where the nitrate yields used do not match the Arey et al. model exactly, but rather are based at least on the number of heavy atoms, and sometimes accounted for double bonds and other effects. An example would be one of the first nitrate formation steps in Peeters et al. 2001, figure 1, formation of RO3, C10 Arey et al. tert nitrate yield 10% 10.45%; C10+O2 tert nitrate yield 11.11%, used yield is rounded 11%.

At that time, it was felt to be sufficient to refer to Arey et al., as the theory-based model was due to be published in full, and it was in many respects a theory-based reparameterization of the Arey et al. model. An unfortunate choice, as ultimately Peeters never published his model, despite extensive hints in in our papers that this was due to happen; the main block was that no theoretical characterization of the nitrite to nitrate interconversion process was ever available, suggested now to be either a roaming reaction or a singlet-triplet-singlet double surface hop, both of which are very hard to do computationally, and thus not characterized even today. Other authors did publish some work on this, e.g. Barker et al. 2003 probed the required energetic and rovibrational characteristics of the nitrite-nitrate interconversion process, but no computationally supported solution was ever found. Other scientists in those days likewise attempted to come up with models based on a quantification of the microscopic mechanism, but all faltered on the lack of a characterization of the nitrite-nitrate conversion step, as well as the odd differences in yields between primary, secondary and tertiary nitrates, which from a theoretical-mechanistic point of view remains unexplained. It may be that some models were presented as talks or posters at some conference, describing these efforts, but my memory does not stretches back that far, and I have only printed proceedings from this period, making searches too time-consuming for a merely historic reminiscence.

While it is possible that Teng et al. were the first to *explicitly* publish this finding in a peer-reviewed paper, the use of heavy atom number instead of carbon number in the prediction of nitrate yields thus dates back about 2 decades. Technically, for theoreticians, Barker et al. 2003 already indicates clearly that heavy atom count is more appropriate than carbon number, as that analysis is based on state density, and essentially only lacks a good description of the nitrite-nitrate conversion. The upcoming results on nitrate yields obtained at NCAR could likewise solve some of the conceptual problems related to prim/sec/tert yields that hampered development of theory-based models.

Feeling old, Luc Vereecken

Response: We thank Luc Vereecken for providing this informative comment. Some of the authors also recall discussions of this type within the EUROTRAC programme, and certainly the idea of

alternatives to carbon number (such as heavy atom number) in the parameterization of nitrate yields and other reactions has also been discussed in MCM meetings from about 10 years ago. We also look forward to further systematic information on the structural dependence of nitrate yields being reported, so that we can do a better job in representing the yields for the variety of structures formed in the future (see also response to Comment E1).

Similarly to yourself, we acknowledge that Teng et al. (2015) were the first to demonstrate the relationship to heavy atom number clearly and explicitly in relation to a systematic set of laboratory experimental data for oxygenated peroxy radicals and therefore feel that it is appropriate to cite that study at the relevant point.

D. Comments by Geoffrey Tyndall (Referee)

Opening comment: This manuscript, the next in a series describing protocols for the automatic generation of chemical mechanisms, addresses the reactions of organic peroxy radicals. Methods are given for the calculation of both overall rate constants and product branching ratios.

The manuscript is detailed, and addresses all or most of the possible reaction partners for RO2 in the atmosphere. This is a lot to cover, and the manuscript is at times a little scant, but in general does a good job at giving enough information to follow what the authors are trying to say.

Response: We are grateful to the referee for these supportive comments on our work. We acknowledge that the primary aim of the manuscript is give the necessary information to allow the estimation methods to be applied, rather than to provide a full review of the topic area. As indicated above (response to Reviewer A, General comments), however, we feel that we have presented an extensive set of information in support of our methods.

I have one relatively minor technical comment, plus a general observation about alkyl nitrate yields, following on from Luc Vereecken's comment.

Comment D1: Page 3, line 18. The first carbon atom in this RO2 radical seems to be missing some bonds. I suspect it is meant to be the oxo dihydroperoxy radical, so C(O)(OOH)CH2. . . etc

Response: Thank you very much for spotting this error (which also occured in Table 1). Quite a few people have read through this manuscript, and you are the first and only person to notice this. We correctly describe the species as a "complex oxo-di-hydroperoxy acyl peroxy radical" in footnote (o) of Table 1, but managed to omit the "oxo" group in the RO_2 structure, which should indeed read "$C(O)(OOH)CH_2CH_2CH_2CH(OOH)C(O)O_2$". This has been corrected in the text and Table 1.

Comment D2 Further thoughts on the temperature dependence of alkyl nitrate yields.

In their 1987 paper, Atkinson et al. [1] parameterized the nitrate yield as a function of temperature and pressure, leading to a pressure dependent term, $Yo(298)*[M]$ multiplied by a temperature dependence $(T/300)^{mo}$ with mo = -2.99, and $Yo(300) = Aexp(n)$, where n is the number of carbon atoms. The high pressure yield in this formulation had a temperature coefficient of -4.69.

In 1989, Carter and Atkinson [2] instead parameterized the ratio ka/kb, and found the best fit with mo = 0, and m(inf) = -8.0. So all the temperature dependence was in the high pressure limit, which leverages the whole curve down to low pressure.

Arey et al. (2001) [3] adopted this latter formulation to extrapolate their room temperature values to other temperatures.

In our 2012 review paper (Orlando and Tyndall, 2012) [4] we attempted to combine the low pressure and temperature dependent terms, using $Yo(298)[M](T/298)$. This is of course erroneous, since if mo=0 the temperature dependence vanishes (other than that implicit in [M]).

It appears that Jenkin et al. (main manuscript Page 4, line 16; SI Page 2) copied our incorrect version in their current manuscript. It is possible that Carter, Atkinson and Arey have updated their fit at some point to include a (T/298) term. However, we cannot remember having seen this anywhere (although we are even older than Dr. Vereecken, and we may have forgotten it).

We apologize for introducing this error into the literature. Note that the formula given in Calvert et al. (2009) "Mechanisms of Atmospheric Oxidation of the Alkanes" is correct, while that in Calvert et al. (2015) "The Mechanisms of Reactions Influencing Atmospheric Ozone" is not.

[1] R. Atkinson, S. M. Aschmann, and A. M. Winer, J. Atmos. Chem., 5 (1987), 91. [2] W. P. L. Carter and R. Atkinson, J. Atmos. Chem., 8 (1989), 165. [3] J. Arey, S. M. Aschmann, E. S. C. Kwok, and R. Atkinson, J. Phys. Chem., A 105 (2001), 1020. [4] J. J. Orlando and G. S. Tyndall, Chem. Soc. Rev., 41 (2012) 6294.

<u>Response</u>: Thank you for communicating this error and for the additional information on where it appears. We have now corrected this, which we understand only requires the removal of the first (T/300) term. Because our example calculations (given in Sect. S1) are all for T = 298 K, this has no effect on the results (to three significant figures).

E. Additional comment on nitrate yields from RO$_2$ + NO from John Crounse and Paul Wennberg (received shortly after the discussion closed)

Comment E1: Do we interpret Table 3 correctly that the recommended beta-OO-OH + NO nitrate yields are based on equally weighted results from OBrien/Shepson, Matsunga/Ziemann, and Teng? The reason we raise this is that we understand there were potential analytical losses of these nitrates in the Shepson and Ziemann studies. In addition, O'Brien apparently did not account for O(^{3}P) chemistry of the alkenes in their 1998 work, which seems to have been important in a number of their experiments. We discussed this in detail here:

https://www.atmos-chem-phys.net/15/4297/2015/acp-15-4297-2015-supplement.pdf

<u>Response</u>: Thank you for this helpful enquiry, and for reminding us of the potential interferences of O(^{3}P) chemistry in the pioneering work of O'Brien, Shepson et al. (1998), as documented by Teng et al. (2015). Our basis for defining the effect of β-hydroxy groups was previously summarised in footnote (c) of Table 3, as follows:

"Based on a compromise of information from O'Brien et al. (1998), Matsunaga and Ziemann (2009; 2010), Yeh and Ziemann (2014b) and Teng et al. (2015) for β-hydroxy substituents, but also taking account of information reported for a number of other oxygenated systems (e.g. Tuazon et al., 1998a; Crounse et al., 2012; Lee et al., 2014) and previous consideration of the OH + isoprene system (Jenkin et al., 2015)."

Having reviewed our procedure, we can confirm that the O'Brien et al. (1998) data were not taken into account, and that reference to it should not have been included in the statement (and has been removed in the revised version of the paper). The yields calculated by our method are actually greater than those reported by O'Brien et al. (1998) by factors of 2 to 3. However, the approach is a compromise between the data reported by Ziemann and co-workers and by Teng et al.. Our calculated yields at the "high *n* plateau" are therefore about a factor of 1.4 greater than those reported by Matsunaga and Ziemann (2009) for linear alkenes, but under-estimate those reported by Teng. et al. (2015) for (lower *n*) terminal alkenes by a similar factor. They do, however, agree well with those reported by Tuazon et al. (1998). We also note that Teng et al. (2015) report lower yields for nitrates formed from internal alkenes (2-methylbut-2-ene, and 2,3-dimethylbut-2-ene). Our method recreates the reported value for 2-methylbut-2-ene very well (10.3 % vs. 9 ± 4 %), and presumably is also consistent with the (unspecified) preliminary lower yield for 2,3-dimethylbut-2-ene compared with hex-1-ene. At present, there is insufficient systematic information to provide different factors for β-hydroxy groups in different environments, such that a single factor is currently

applied to those formed from terminal acyclic alkenes, internal acyclic alkenes and cycloalkenes. We regard this as a reasonable compromise based on currently reported data, which can hopefully be improved upon when systematic data from a larger number of precursor alkenes/cycloalkenes is available. Ideally, such data would also allow the underlying function (based on Arey et al., 2001) to be optimised for different peroxy radical classes.

The Teng et al. (2015) data for β-hydroxy nitrates from terminal alkenes suggest no reduction in yield compared with those for alkyl nitrates containing the same number of heavy atoms. We considered using this as the basis for the effect of the beta-hydroxy group, but found that the calculated yields would overestimate those reported in almost all other studies. For example, the total calculated nitrate yield from OH + α-pinene would be about 29 %, compared with the reported value of (18 ± 9) % (Noziere et al, 1999) - and a gross overestimate of the 3.3 % hydroxynitrate yield reported very recently by Xu et al. (2019) (although we did not know that at the time). Similarly, the calculated nitrate yield from OH + isoprene at atmospheric pressure and the high NO limit (16 %) would be slightly outside the range of reported yields (4.4 - 14 %), although we recognise that the true value is likely towards the high end of the reported range.

As a result of this discussion, we have now included the following point in our recommendations list in Sect. 4:

"Further systematic data on $RONO_2$ yields from the reactions with NO are required, to help improve branching ratio parameterizations. These include additional data for a variety of acyclic and cyclic oxygenated RO_2 as a function of size and structure."

References

Arey, J., Aschmann, S. M., Kwok, E. S. C., and Atkinson, R.: Alkyl nitrate, hydroxyalkyl nitrate, and hydroxycarbonyl formation from the NO_x–air photooxidations of C_5–C_8 n-alkanes, J. Phys. Chem. A, 105, 1020–1027, doi:10.1021/jp003292z, 2001.

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, 2005.

Calvert, J. G., Orlando, J. J., Stockwell, W. R. and Wallington, T. J.: The mechanisms of reactions influencing atmospheric ozone, Oxford University Press, Oxford. ISBN 978-0-19-023301-0, 2015.

Caravan, R. L., Khan, M. A. H., Zádor, J., Sheps, L., Antonov, I. O., Rotavera, B., Ramasesha, K., Kendrew, A., Chen, M., Rösch, D., Osborn, D. L., Fittschen, C., Schoemaecker, C., Duncianu, M., Grira, A., Dusanter, S., Tomas, A., Percival, C., Shallcross, D. E. and Taatjes, C. A.: The reaction of hydroxyl and methylperoxy radicals is not a major source of atmospheric methanol, Nat. Commun., 9, Article number 4343, https://doi.org/10.1038/s41467-018-06716-x, 2018.

Elrod, M. J.: Kinetics study of the aromatic bicyclic peroxy radical + NO Reaction: overall rate constant and nitrate product yield measurements, J. Phys. Chem. A, 115, 8125–8130, 2011.

Hui, A. O., Fradet, M., Okumura, M., and Sander, S. P.: Temperature dependence study of the kinetics and product yields of the HO_2 + $CH_3C(O)O_2$ Reaction by Direct Detection of OH and HO_2 radicals using 2f-IR wavelength modulation spectroscopy, J. Phys. Chem. A, doi: 10.1021/acs.jpca.9b00442, 2019.

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(1), 81-104, 1997.

Jenkin, M. E., Young, J. C., and Rickard, A. R.: The MCM v3.3.1 degradation scheme for isoprene, Atmos. Chem. Phys., 15, 11433-11459, doi:10.5194/acp-15-11433-2015, 2015.

Jenkin, M. E., Valorso, R., Aumont, B., Rickard, A. R., and Wallington, T. J.: Estimation of rate coefficients and branching ratios for gas-phase reactions of OH with aliphatic organic compounds for use in automated mechanism construction, Atmos. Chem. Phys., 18, 9297-9328, https://doi.org/10.5194/acp-18-9297-2018, 2018.

Li, J., Cleveland, M., Ziemba, L. D., Griffin, R. J., Barsanti, K. C., Pankow, J. F., and Ying, Q.: Modeling regional secondary organic aerosol using the Master Chemical Mechanism, Atmos. Environ., 102, 52-61, 2015.

Matsunaga, A. and Ziemann, P. J.: Yields of beta-hydroxynitrates and dihydroxynitrates in aerosol formed from OH radical initiated reactions of linear alkenes in the presence of NOx , J. Phys. Chem. A, 113, 599–606, doi:10.1021/jp807764d, 2009.

Matsunaga, A. and Ziemann, P. J.: Yields of beta-hydroxynitrates, dihydroxynitrates, and trihydroxynitrates formed from OH radical-initiated reactions of 2-methyl-1-alkenes, P. Natl. Acad. Sci. USA, 107, 6664–6669, doi:10.1073/pnas.0910585107, 2010.

Nozière, B. and Hanson, D.: Speciated monitoring of gas-phase organic peroxy radicals by chemical ionization mass spectrometry: Cross-reactions between CH_3O_2, $CH_3(CO)O_2$, $(CH_3)_3CO_2$, and c-$C_6H_{11}O_2$, J. Phys. Chem. A, 121, 8453-8464, 2017.

Nozière, B. . Barnes, I. and Becker, K. H.: Product study and mechanisms of the reactions of α-pinene and of pinonaldehyde with OH radicals, J. Geophys. Res., 104 (D19), 23,645-23,656, 1999.

O'Brien, J. M., Czuba, E., Hastie, D. R., Francisco, J. S., and Shepson, P. B.: Determination of the hydroxy nitrate yields from the reaction of C_2–C_6 alkenes with OH in the presence of NO, J. Phys. Chem. A, 102, 8903–8908, doi:10.1021/jp982320z, 1998.

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, 2012.

Saunders, S. M., Jenkin, M. E., Derwent, R. G. and Pilling, M. J.: Protocol for the development of the Master Chemical Mechanism, MCM v3 (Part A): tropospheric degradation of non-aromatic volatile organic compounds, Atmos. Chem. Phys., 3, 161-180, 2003.

Teng, A. P., Crounse, 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.

Tuazon, E. C., Aschmann, S. M., Arey, J., and Atkinson, R.: Products of the gas-phase reactions of a series of methyl-substituted ethenes with the OH radical, Environ. Sci. Technol., 32, 2106-2112, 1998.

Vereecken, L., Aumont, B., Barnes, I., Bozzelli, J. W., Goldman, M. J., Green, W. H., Madronich, S., McGillen, M. R., Mellouki, A., Orlando, J. J., Picquet-Varrault, B., Rickard, A. R., Stockwell, W. R., Wallington, T. J. and Carter, W. P. L.: Perspective on mechanism development and structure-activity relationships for gas-phase atmospheric chemistry, Int. J. Chem. Kinet., 50, 435-469, 2018.

Wennberg, P. O., Bates, K. H., Crounse, J. D., Dodson, L. G., McVay, R. C., Mertens, L. A., Nguyen, T. B., Praske, E., Schwantes, R. H., Smarte, M. D., St Clair, J. M., Teng A. P., Zhang, X. and Seinfeld, J. H.: Gas-phase reactions of isoprene and its major oxidation products, Chem. Rev., 118 (7), 3337-3390, 2018.

Xu, L., Møller, K. H., Crounse, J. D., Otkjær, R. V., Kjaergaard, H. G., and Wennberg, P. O.: Unimolecular reactions of peroxy radicals formed in the oxidation of α-pinene and β-pinene by hydroxyl radicals, J. Phys. Chem. A., 123 (8), 1661-1674, doi: 10.1021/acs.jpca.8b11726, 2019.