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 is more often used to model specific experiments such as environmental chambers or lab studies, where CH3O2 is not necessarily the dominant proxy radical, if it is present at all in non-negligible concentration.

In many studies, only one or a few primary VOCs are present, and the RO2 population pool is heavily biased towards one or a few of the reactivity classes presented in the SI, especially in the early stages of the oxidation. Such consideration might be mentioned in the main paper. For me personally, given what I perceive as the main use of mechanisms of the envisioned detail, the most logical choice would be to separate the RO2 pool into reactivity classes.

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.

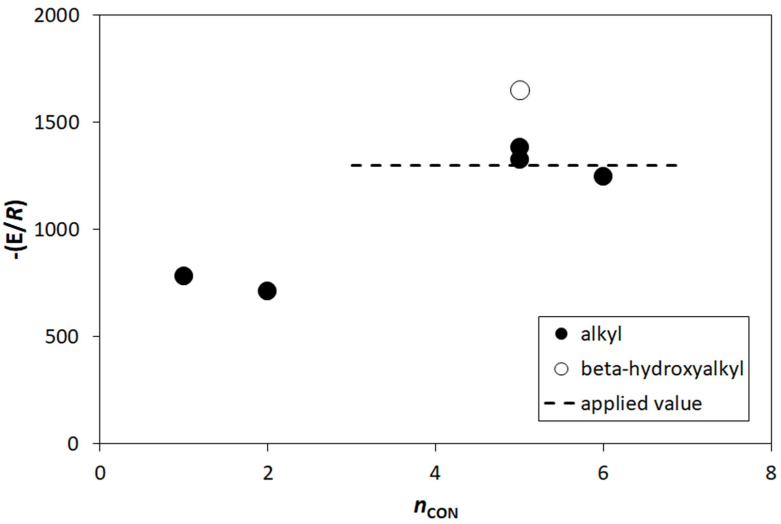

Fig. R1 Temperature coefficients for reactions of alkyl and β-hydroxyalkyl RO_2 radicals with HO_2 as a function of n_{CON}.

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, $E/R = -(720 \pm 170)$ 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:

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

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

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

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

Response: 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 $O(^3P)$ 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

Response: Thank you for this helpful enquiry, and for reminding us of the potential interferences of $O(^3P)$ 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.”

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Estimation of rate coefficients and branching ratios for reactions of organic peroxy radicals for use in automated mechanism construction

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Abstract.

Organic peroxy radicals (RO_2), formed from the degradation of hydrocarbons and other volatile organic compounds (VOCs), play a key role in tropospheric oxidation mechanisms. Several competing reactions may be available for a given RO_2 radical, the relative rates of which depend on both the structure of RO_2 and the ambient conditions. Published kinetics and branching ratio data are reviewed for the bimolecular reactions of RO_2 with NO, NO_2, NO_3, OH and HO_2; and for their self-reactions and cross-reactions with other RO_2 radicals. This information is used to define generic rate coefficients and structure-activity relationship (SAR) methods that can be applied to the bimolecular reactions of a series of important classes of hydrocarbon and oxygenated RO_2 radical. Information for selected unimolecular isomerization reactions (i.e. H-atom shift and ring-closure reactions) is also summarised and discussed. The methods presented here are intended to guide the representation of RO_2 radical chemistry in the next generation of explicit detailed chemical mechanisms.

1 Introduction

Organic peroxy radicals (RO_2) are important intermediates in the tropospheric degradation of hydrocarbons and other volatile organic compounds (VOCs). It is well established that their chemistry plays a key role in the mechanisms that generate ozone (O_3), secondary organic aerosol (SOA) and other secondary pollutants (e.g. Lightfoot et al., 1992; Jenkin and Clemitshaw, 2000; Tyndall et al., 2001; Archibald et al., 2009; Orlando and Tyndall, 2012; Ehn et al., 2017), and rigorous representation of their chemistry is therefore essential for chemical mechanisms used in chemistry-transport models. As discussed in the preceding papers in this series (Jenkin et al., 2018a; 2018b), they are formed rapidly and exclusively from the reactions of O_2 with the majority of carbon-centred organic radicals (R) (reaction R1), these in turn being produced from the reactions that initiate VOC degradation (e.g. reaction with OH radicals), or from other routes, such as decomposition of larger oxy radicals (M denotes a third body, most commonly N_2 or O_2 under atmospheric conditions):

$R + O_2 (+M) \rightarrow RO_2 (+M)$ (R1)

Under tropospheric conditions, a given RO_2 radical may have several competing reactions available, the relative rates of which are dependent both on the prevailing ambient conditions and on the structure of RO_2. These include a series of bimolecular reactions (i.e. with NO, NO_2, NO_3, OH and HO_2; and the self-reaction and cross-reactions with the multitude of other RO_2 radicals present in the atmosphere), which are generally available for all RO_2 radicals; and specific unimolecular isomerization reactions (i.e. H-atom shift or ring-closure reactions), that are potentially available for some classes of RO_2.

The propagating channel of the reaction of RO_2 with NO (reaction R2a) plays a key role in tropospheric O_3 formation, through oxidising NO to NO_2, and also usually represents the major reaction for RO_2 radicals under comparatively polluted conditions:

$RO_2 + NO \rightarrow RO + NO_2$ (R2a)

The efficiency of this reaction is influenced by the relative importance of the other reactions available for a given RO_2 radical. The contribution of the terminating channel of the reaction of RO_2 with NO (forming an organic nitrate product, $RONO_2$) depends on the structure and size of RO_2; and the reaction of NO_2 with selected RO_2 radicals forms stable peroxynitrate products, $ROONO_2$. The formation, transport and degradation of these oxidised organic nitrogen reservoirs from the RO_2 + NO and RO_2 + NO_2 reactions has potential impacts in a number of ways, ranging from the inhibition of O_3 formation on local/regional scales to influencing the global budget and distribution of NO_x and O_3 (e.g. Perring et al., 2013).

The reactions of RO_2 radicals with NO_3 primarily play a role during the night-time in moderately polluted air, providing a radical propagation route that potentially supplements night-time chain oxidation processes (e.g. Carslaw et al., 1997; Bey et al., 2001a; 2001b; Geyer et al., 2003; Walker et al., 2015).

The reactions with OH, HO_2 and the pool of RO_2 radicals gain in importance as the availability of NO_x becomes more limited, and therefore also inhibit O_3 formation by competing with reaction (R2a). In many cases, the reactions are significantly terminating and collectively make a major contribution to controlling atmospheric free radical concentrations under NO_x-limited conditions, although the branching ratios for the propagating and terminating reaction channels depend on the structure of RO_2. For some classes of RO_2, unimolecular isomerization reactions can compete with (or dominate over) the bimolecular reactions. These reactions therefore potentially play an important role in HO_x radical recycling under NO_x-limited conditions, and in rapid chain oxidation mechanisms generating highly oxidised multifunctional molecules, HOMs (e.g. Peeters et al., 2009; 2014; Crounse et al., 2013; Ehn et al., 2014; 2017; Jokinen et al., 2014; Rissanen et al., 2015; Bianchi et al., 2019). The relative contributions of the various reactions available for RO_2 thus influence the distribution and functional group content of the oxidized products formed, and their physicochemical properties (e.g. volatility and solubility), and therefore the SOA formation propensity of the chemistry.

In this paper, published data on the kinetics and branching ratios for the above bimolecular reactions of hydrocarbon and oxygenated RO_2 radicals~~, and for selected unimolecular isomerization reactions,~~ 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) to guide the representation of the RO_2 reactions in future detailed chemical mechanisms (Vereecken et al., 2018). In particular, the methods presented below are being used to design the next generation of explicit mechanisms based on the Generator for Explicit Chemistry and Kinetics of Organics in the Atmosphere, GECKO-A (Aumont et al., 2005), and the Master Chemical Mechanism, MCM (Saunders et al., 2003). Application of the methods is illustrated with examples in the supporting information provided in the Supplement.

2 Bimolecular reactions of RO_2 radicals

2.1 The reactions of RO_2 with NO

2.1.1 Kinetics

Rate coefficients for the reactions of NO with a variety of specific hydrocarbon and oxygenated RO_2 radicals have been reported, as summarized in Table 1. For the vast majority of the RO_2 radicals formed in detailed mechanisms, however, kinetic data are unavailable, and it is therefore necessary to assign generic rate coefficients based on the reported data.

For acyl peroxy radicals (i.e. of structure $RC(O)O_2$), a generic rate coefficient (k_{APNO}) is applied:

$$k_{\mathrm{APNO}} = 7.5 \times 10^{-12} \exp(290/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \qquad (1)$$

This is based on the IUPAC Task Group[1] recommendation for the reaction of NO with $CH_3C(O)O_2$. As shown in Table 1, this is also close to the rate coefficients recommended for the less studied acyl peroxy radicals, $C_2H_5C(O)O_2$ and $CH_2{=}CH(CH_3)C(O)O_2$. The 298 K value reported for ~~CH~~C(O)(OOH)$CH_2CH_2CH_2CH(OOH)C(O)O_2$ (Berndt et al., 2015) is also broadly consistent with k_{APNO}, although further studies of highly-oxygenated acyl peroxy radicals would help to establish the effects of additional substituent groups.

For other classes of hydrocarbon and oxygenated peroxy radical, a generic rate coefficient (k_{RO2NO}) is applied:

$$k_{\mathrm{RO2NO}} = 2.7 \times 10^{-12} \exp(360/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \qquad (2)$$

The value of k_{RO2NO} at 298 K (9.0×10^{-12} cm^3 molecule^{-1} s^{-1}) is based on a rounded average of the 298 K rate coefficients listed for the ≥ C_2 alkyl, cycloalkyl, hydroxyalkyl, hydroxyalkenyl, oxoalkyl, hydroxy-oxyalkyl and hydroxy-dioxa-bicyclo RO_2 radicals in Table 1, which show no significant trends related to the identity and structure of R. The temperature dependence is similarly based on the rounded average of the available values within this group, which are limited to those for $C_2H_5O_2$, n-$C_3H_7O_2$ and i-$C_3H_7O_2$. In practice, the preferred values for all the ≥ C_2 (non-acyl) RO_2 radicals in Table 1 are also equivalent to k_{RO2NO} within the reported uncertainties, such that the generic rate coefficient can reasonably be applied for simplicity in all cases except

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[1] The "IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation" is abbreviated to "IUPAC Task Group" for simplicity. The evaluation is available at http://iupac.pole-ether.fr/ (access date January 2019 throughout).

CH_3O_2. Although derived from a more extensive dataset, the expression for k_{RO2NO} in Eq. (2) is identical to that recommended previously by Atkinson (1997).

2.1.2 Product branching ratios

The following channels are considered for the reactions of RO_2 with NO:

$$RO_2 + NO \rightarrow RO + NO_2 \quad (R2a)$$

$$RO_2 + NO\ (+M) \rightarrow RONO_2\ (+M) \quad (R2b)$$

It is well established that the branching ratio for alkyl peroxy radicals depends on temperature, pressure, and the size and degree of substitution of the peroxy radical (e.g. Carter and Atkinson, 1989; Arey et al., 2001; Yeh and Ziemann, 2014a). The branching ratio has also been reported to be influenced by the presence of oxygenated substituents, with most systematic information reported for β- and δ- hydroxy groups (e.g. O'Brien et al., 1998; Matsunga and Ziemann, 2009, 2010; Yeh and Ziemann, 2014b; Teng et al., 2015).

The fraction of the reaction forming a nitrate product ($RONO_2$) via the terminating channel, $R_{2b} = k_{2b}/(k_{2a}+k_{2b})$, is calculated following the method originally reported for secondary alkyl peroxy radicals by Carter and Atkinson (1989), and subsequently updated by Arey et al. (2001) and Teng et al. (2015). Based on this method~~, and adopting the terminology used by Orlando and Tyndall (2012)~~, the reference branching ratio for secondary alkyl peroxy radicals, $R° = (k_{2b}/k_{2a})°$ is calculated as follows,

$$R° = [A/(1 + (A/B))]\ F^{z} \quad (3)$$

with $A = 2 \times 10^{-22} \exp(n_{CON})\ [M]$ ~~$(T/300)$~~, $B = 0.43\ (T/300)^{-8}$, $F = 0.41$, and $z = (1 + (\log_{10}(A/B))^2)^{-1}$. 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}).

The fractions of the reaction proceeding via the terminating channel, R_{2b}, and the propagating channel, R_{2a} (= $1-R_{2b}$), for a specific peroxy radical are then given by:

$$R_{2b} = f_a f_b\ (R°/(1+R°)) \quad (4)$$

The effect of the degree of substitution (i.e. whether the radical is primary, secondary or tertiary) is described by f_a, with a unity value applied to secondary peroxy radicals, by definition. A further scaling factor, f_b, is used to describe systematic variations in the yields of $RONO_2$ resulting from the presence of oxygenated substituents (e.g. the effect of hydroxyl substituents, as indicated above), or for specific peroxy radical classes, with a value of f_b being required to account for the effect of each relevant substituent. The applied values of f_a and f_b are summarized in Tables 2 and 3, and example calculations are provided in Sect. S1.

It is also recognised that channel (R2a) is significantly exothermic, such that prompt decomposition or isomerization of a fraction of the initially-formed chemically activated oxy radicals has been reported to occur in some cases; with the remainder being collisionally deactivated to form thermalized RO (e.g. Orlando et al., 2003; Calvert et al., 2015). This is particularly important for β-hydroxy-oxy radicals (e.g. Orlando et al., 1998; Vereecken et al., 1999; Vereecken and Peeters, 1999; Caralp et al., 2003) and some other oxygenated oxy radicals (e.g. Christensen et al., 2000; Orlando et al., 2000; Wallington et al., 2001). The contributions and treatment of these reactions is summarized in Sect. S2.

2.2 The reaction of RO_2 with NO_2

The reactions of RO_2 with NO_2 have generally been reported to proceed via a reversible association reaction in each case to form a peroxy nitrate ($ROONO_2$):

$$RO_2 + NO_2 \ (+M) \rightleftharpoons ROONO_2 \ (+M) \qquad \text{(R3a)}$$

Rate coefficients for the forward and reverse reactions for a number of RO_2 radicals are summarized in Table 4. Those for CH_3O_2 and $C_2H_5O_2$, and for the two simplest acyl peroxy radicals, $CH_3C(O)O_2$ and $C_2H_5C(O)O_2$, are based on (or informed by) the IUPAC Task Group recommendations, and describe the pressure and temperature dependences of the reactions. In all other cases, the reactions are assumed to be at the high pressure limit under atmospheric conditions, and generic parameters are applied. The parameters $k_{\mathrm{f\,PN}}$ and $k_{\mathrm{b\,PN}}$ (given in Table 4) can reasonably be applied to reactions involving non-acyl peroxy radicals, being based on the high pressure limiting rate coefficients (k_∞) for the forward and reverse reactions of $C_2H_5O_2$ and those reported for a number of higher alkyl peroxy radicals at close to atmospheric pressure (see Table 4 comments). This assumption is also broadly consistent with the limited information available for the forward or reverse reactions of other non-acyl oxygenated peroxy radicals (e.g. Orlando and Tyndall, 2012). In practice, however, these reactions are often omitted from atmospheric chemical mechanisms, owing to the instability of the $ROONO_2$ products under lower tropospheric conditions (lifetime ≈ 0.2 s at 298 K). As a result, only the formation and decomposition of methyl peroxy nitrate, CH_3OONO_2, from the most abundant non-acyl peroxy radical, CH_3O_2, have previously been represented in the MCM (Saunders et al., 2003). This approach remains advocated here for application to lower tropospheric conditions.

The reactions are generally represented for acyl peroxy radicals, for which the product peroxyacyl nitrates, $RC(O)OONO_2$, are particularly stable (lifetime ≈ 40 – 50 minutes at 298 K). The generic parameters, $k_{\mathrm{f\,PAN}}$ and $k_{\mathrm{b\,PAN}}$, are applied in the majority of cases (see Table 4). As shown in Fig. 1, larger acyl peroxy radicals have been reported to be slightly more stable than those derived from $CH_3C(O)O_2$ and $C_2H_5C(O)O_2$ (Roberts and Bertman, 1992; Kabir et al., 2014), and the assigned value of $k_{\mathrm{b\,PAN}}$ is consistent with the data for the larger species.

Reported data for $CH_3OC(O)O_2$, $C_6H_5OC(O)O_2$ and $C_2H_5OC(O)O_2$ (Kirchner et al., 1999; Bossolasco et al., 2011) indicate a reduced thermal stability of peroxyacyl nitrates derived from formate esters, and an increased decomposition rate ($2 \times k_{\mathrm{b\,PAN}}$) is therefore applied to $ROC(O)OONO_2$ species in general.

In a limited number of cases, the reaction of RO_2 with NO_2 has been reported to oxidize NO_2 to NO_3 in an irreversible reaction:

$RO_2 + NO_2 \rightarrow RO + NO_3$ (R3b)

These cases include $HC(O)C(O)O_2$ (Orlando and Tyndall, 2001), $CH_3C(O)C(O)O_2$ (Jagiella and Zabel, 2008) and the phenylperoxy radical, $C_6H_5O_2$ (Jagiella and Zabel, 2007). Reaction (R3b) is therefore applied generally to $HC(O)C(O)O_2$, $RC(O)C(O)O_2$, $C_6H_5O_2$ and ~~substituted phenyl~~other aryl peroxy radicals, using the generic rate coefficient k_{fPAN}.

2.3 The reaction of RO_2 with NO_3

On the basis of reported information for CH_3O_2 and $C_2H_5O_2$ (e.g. Biggs et al., 1995; Kukui et al., 1997), the reactions of RO_2 with NO_3 are assumed to proceed via a single channel in each case, as follows:

$RO_2 + NO_3 \rightarrow RO + NO_2 + O_2$ (R4)

Reported rate coefficients are summarised in Table 5. The reaction of $C_2H_5O_2$ with NO_3 is the most studied, with consistent 298 K rate coefficients reported in a number of studies (Biggs et al., 1995; Ray et al., 1996; Vaughan et al., 2006; Laversin et al., 2016) and with the temperature dependence systematically investigated (Laversin et al., 2016). The corresponding parameters in Table 5 therefore form the basis of a generic rate coefficient for the reactions of non-acyl peroxy radicals with NO_3:

$$k_{\mathrm{RO2NO3}} = 8.9 \times 10^{-12} \exp(-390/T)\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}} \quad (5)$$

Within the reported uncertainties, the value of the rate coefficient at 298 K is consistent with that for c-$C_6H_{11}O_2$ and with the approximate value for c-$C_5H_9O_2$ reported by Vaughan et al. (2006); and the temperature dependence expression for k_{RO2NO3} is consistent with those reported for the oxygenated primary peroxy radicals, $(CH_3)_2C(OH)CH_2O_2$, $CH_3OCH_2O_2$ and $CH_3C(O)CH_2O_2$, by Kalalian et al. (2018). k_{RO2NO3} is therefore currently considered appropriate for application to all $\geq C_2$ non-acyl peroxy radicals. For CH_3O_2, the reaction has been well studied at 298 K, and the value in Table 5 is applied in conjunction with the k_{RO2NO3} pre-exponential factor, leading to:

$$k(CH_3O_2 + NO_3) = 8.9 \times 10^{-12} \exp(-600/T)\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}} \quad (6)$$

The generic rate coefficient for acyl peroxy radicals is based on data for $CH_3C(O)O_2$, which has been shown to react slightly more rapidly with NO_3 (Canosa-Mas et al., 1996; Doussin et al., 2003). The value at 298 K in Table 5 (based on that reported by Doussin et al., 2003) is once again applied in conjunction with the k_{RO2NO3} pre-exponential factor, leading to:

$$k_{\mathrm{APNO3}} = 8.9 \times 10^{-12} \exp(-305/T)\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}} \quad (7)$$

The resultant weak temperature dependence yields a value of k_{APNO3} in the range 403-443 K that is fully consistent with that reported by Canosa-Mas et al. (1996).

2.4 The reaction of RO_2 with OH

Kinetics determinations have been reported for the reactions of OH with C_1-C_4 alkyl peroxy radicals. As shown in Table 6, these reactions are reported to occur rapidly at room temperature, with the rate coefficients for all the reactions being essentially equivalent at 298 K, within the reported uncertainties. Based on the study of Yan et al. (2016), a weak temperature dependence is recommended for the reaction of CH_3O_2 with OH, and the resultant expression,

$$k_{RO2OH} = 3.7 \times 10^{-11} \exp(350/T)\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}} \quad (8)$$

is also adopted in the present work as a generic rate coefficient for the reactions of RO_2 with OH.

The following product channels are considered, but with their branching ratios being strongly dependent on the size of R:

$$RO_2 + OH \rightarrow RO + HO_2 \quad (R5a)$$

$$RO_2 + OH \rightarrow ROH + O_2 \quad (R5b)$$

$$RO_2 + OH\ (+M) \rightarrow ROOOH\ (+M) \quad (R5c)$$

In their theoretical studies of the reaction of CH_3O_2 with OH, Bian et al. (2015), Müller et al. (2016) and Assaf et al. (2018) calculated channel (R5a) to be the most favourable, with experimental confirmation of a dominant contribution from this channel reported for CH_3O_2 by Assaf et al. (2017a; 2018). A number of alternative channels have been considered in modelling assessments (e.g. Archibald et al., 2009), including formation of CH_2O_2 and H_2O or CH_3OH and O_2. 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). The formation of CH_3OH and O_2 via channel (R5b) has been shown to make a minor contribution (6 – 9 %) in the experimental study of Caravan et al. (2018), consistent with the theoretical estimate of ~ 7 % by Müller et al. (2016). 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). As a result, values of $k_{5a}/k_5 = 0.93$ and $k_{5b}/k_5 = 0.07$ are currently assigned to the reaction of CH_3O_2 with OH in the present work.

The experimental and theoretical study of Assaf et al. (2018) for a series of C_1-C_4 alkyl peroxy radicals has demonstrated that the reaction can more generally be regarded as proceeding by either channel (R5a) or (R5c). Formation of the thermalized hydrotrioxide, ROOOH, via channel (R5c) was found to be increasingly important for the larger RO_2. Based approximately on their theoretical calculations for 298 K and 1 atmosphere pressure, k_{5c}/k_5 is thus currently assigned a value of 0.0 for CH_3O_2, 0.8 for RO_2 for which $n_{CON} = 2$ (e.g. $C_2H_5O_2$ and $HOCH_2O_2$) and 1.0 for all other RO_2 radicals. In the $n_{CON} = 2$ case, the balance of the reaction is assigned to channel (R5a), i.e. with $k_{5b}/k_5 = 0$. As discussed by Assaf et al. (2018), detailed experimental and theoretical studies of the atmospheric fate of ROOOH are therefore clearly required for the effect of the RO_2 + OH reaction to be fully assessed and represented. A provisional treatment is provided in Sect. S3, based mainly on rate coefficients reported in the theoretical studies of Müller et al. (2016), Assaf et al. (2018) and Anglada and Solé (2018).

2.5 The reaction of RO_2 with HO_2

2.5.1 Kinetics

Rate coefficients for the reactions of HO_2 with a variety of specific hydrocarbon and oxygenated RO_2 radicals have been reported, as summarized in Table 7. For the vast majority of the RO_2 radicals formed in detailed mechanisms, however, kinetic data are unavailable, and it is therefore necessary to assign generic rate coefficients based on the reported data.

As discussed previously (Jenkin et al., 1997; Saunders et al., 2003; Boyd et al., 2003a; Orlando and Tyndall, 2012), the 298 K rate coefficients tend to increase with the size of the organic group. Fig. 2 shows the data plotted as a function of n_{CON}. The data for alkyl peroxy radicals and β-hydroxyalkyl peroxy radicals (the most systematically studied groups) show comparable values across the n_{CON} range. Based on optimization to these data, the following expression is derived for application to non-acyl peroxy radicals:

$$k_{\mathrm{RO2HO2}} = 2.8 \times 10^{-13} \exp(1300/T)\,[1-\exp(-0.23 n_{\mathrm{CON}})]\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}} \quad (9)$$

The temperature dependence is typical of that reported for > C_2 alkyl and β-hydroxy RO_2 radicals, and remains unchanged from that applied previously by Saunders et al. (2003).

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} = ~~6.3~~3.6 $\times 10^{-12}$ exp(~~580~~720/T) [1-exp(-0.23n_{CON})] cm^3 molecule^{-1} s^{-1}
(10)

2.5.2 Product branching ratios

On the basis of reported information, the following channels are considered for the reactions of RO_2 with HO_2:

$RO_2 + HO_2 \rightarrow ROOH + O_2$ (R6a)

$\rightarrow ROH + O_3$ (R6b)

$\rightarrow R_{-H}=O + H_2O + O_2$ (R6c)

$\rightarrow RO + OH + O_2$ (R6d)

$\rightarrow R_{\text{-H}}=O + OH + HO_2$ (R6e)

Formation of a hydroperoxide product (ROOH) and O_2 via terminating channel (R6a) is reported to be dominant for reactions of alkyl peroxy radicals, and this is also taken to be the default where no information is available (see Table 8). However, the reactions of HO_2 with oxygenated peroxy radicals have received considerable attention, and evidence has been reported for several additional channels leading to both radical termination, (R6b) and (R6c), and radical propagation, (R6d) and (R6e). Table 8 summarizes the 298 K branching ratios that are applied to several classes of oxygenated peroxy radical, based on reported information.

The temperature-dependences of the reaction channels have generally not been studied, and the branching ratios in Table 8 are thus applied independent of temperature in most cases. The only exception is the reaction of HO_2 with (non-~~phenyl~~aryl) acyl peroxy radicals. 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:~~The temperature dependence of k_{6a}/k_{6b} is defined using the experimental characterization of the $CH_3C(O)O_2 + HO_2$ reaction reported by Horie and Moortgat (1992), with k_{6d}/k_{6b} provisionally based on the results of the theoretical calculations of Hasson et al. (2005) for the same reaction between 250 K and 300 K at atmospheric pressure:~~

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

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

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

~~$k_{6a}/k_{6b}\ (RC(O)O_2) = 3.4 \times 10^{2} \exp(-1430/T)$ (11)~~

~~$k_{6d}/k_{6b}\ (RC(O)O_2) = 2.34 \times 10^{4} \exp(-2600/T)$ (12)~~

The corresponding temperature dependences of the channel ~~branching ratios (k_{6a}/k_6, k_{6b}/k_6 and k_{6d}/k_6)~~rate coefficients, derived from the $CH_3C(O)O_2$ data, are thus applied to all (non-~~phenyl~~aryl) acyl peroxy radicals. The variation of the branching ratios and channel rate coefficients ~~is~~ are illustrated for the $CH_3C(O)O_2 + HO_2$ reaction in Figs. S2 and S3, for the ~~250~~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 ~~The temperature dependence of OH formation, described by k_{6d}/k_6, was used to correct the temperature coefficient applied to the overall~~

~~reaction kinetics, because the effect of the resultant reagent radical regeneration was not taken into account in reported studies of the temperature dependence of the $CH_3C(O)O_2 + HO_2$ reaction~~ (see Sect. S4 for further details).

2.6 The permutation reactions of RO_2

The “permutation” reactions of a given RO_2 radical are its self-reaction (R7), and its cross-reactions (R8) with other peroxy radicals, R’O_2, for which a number of product channels may occur:

$RO_2 + RO_2 \rightarrow RO + RO + O_2$ (R7a)

$\rightarrow R_{-H}{=}O + ROH + O_2$ (R7b)

$\rightarrow ROOR + O_2$ (R7c)

$RO_2 + R'O_2 \rightarrow RO + R'O + O_2$ (R8a)

$\rightarrow R_{-H}{=}O + R'OH + O_2$ (R8b)

$\rightarrow R'_{-H}{=}O + ROH + O_2$ (R8c)

$\rightarrow ROOR' + O_2$ (R8d)

In view of the large number of RO_2 radicals generated in a detailed chemical mechanism, however, it is unrealistic to represent these reactions explicitly, and the use of simplified parameterizations is essential (Madronich and Calvert, 1990). As described in detail previously (Jenkin et al., 1997), a very simplified approach has traditionally been adopted in the MCM, in which each peroxy radical is assumed to react with all other peroxy radicals (i.e. the peroxy radical “pool”) at a single, collective rate. This is achieved by defining a parameter “$\Sigma[RO_2]$” which is the sum of the concentrations of all peroxy radicals, excluding HO_2. The collective rate of all the permutation reactions of a particular peroxy radical is then represented by a single pseudo-unimolecular reaction, which has an assigned rate coefficient equal to $k_9 \times \Sigma[RO_2]$,

$RO_2 \rightarrow \text{products}$ (R9)

with the value of k_9 depending on the structure of the reacting RO_2 radical. A similar, but more detailed, approach has been applied in GECKO-A, in which the peroxy radical population is divided into a number of reactivity classes (Aumont et al., 2005). This requires the inclusion of a pseudo-unimolecular reaction (analogous to reaction (R9)) for reaction of a given peroxy radical with each peroxy radical class, but has the advantage that differential reactivity with each of those classes can be represented, as appropriate. The following ~~paragraphs~~ sub-sections describe the basis for assigning~~how~~ rate parameters ~~are assigned~~ to the single parameterized permutation reactions (reaction (R9)) for each peroxy radical in the more simplified MCM approach. Extension of the method to reactions with a number of reactivity classes (as traditionally applied with GECKO-A) is described in Sect. S5.

2.6.1 Kinetics of self-reactions

Rate coefficients for the self-reactions and cross-reactions of a variety of specific hydrocarbon and oxygenated RO_2 radicals have been reported (as summarized in Tables 9-11), and these form the basis of assigning rate parameters to the parameterized permutation reaction (reaction (R9)) for each peroxy radical. The data show that the self-reaction reactivity, relative to that of alkyl peroxy radicals, is activated by the presence of numerous functional groups (including allyl-, benzyl-, hydroxy-, alkoxy-, oxo- and acyl-), and that the rate coefficients follow the general trend of decreasing reactivity, primary > secondary > tertiary, for peroxy radicals containing otherwise similar functionalities. It also appears that reactivity tends to increase with the size of the organic group towards a "plateau" value, as most clearly demonstrated by the systematic study of secondary alkyl peroxy radicals reported by Boyd et al. (1999). Based on optimization to the complete secondary alkyl peroxy radical dataset, an expression almost identical to that recommended by Boyd et al. (1999) is thus derived as a reference rate coefficient for secondary peroxy radicals at 298 K, as illustrated in Fig. 3 (units of k are cm^3 $molecule^{-1}$ s^{-1}) :

$$\log_{10}(k^\circ_{RO2RO2(sec)}) = -12.9-(3.2 \times \exp[-0.64(n_{CON}-2.3)]) \qquad (~~13~~14)$$

The data for primary alkyl peroxy radicals are more limited. Those for $C_2H_5O_2$, n-$C_3H_7O_2$, i-$C_4H_9O_2$ and neo-$C_5H_{11}O_2$ suggest a similar trend for primary alkyl peroxy radicals, and an analogous expression to Eq. (~~13~~14) is therefore derived as a reference rate coefficient at 298 K (see Fig. 3):

$$\log_{10}(k^\circ_{RO2RO2(prim)}) = -11.7-(3.2 \times \exp[-0.55(n_{CON}-0.52)]) \qquad (~~14~~15)$$

It is noted, however, that rate coefficients for the self-reactions of n-$C_4H_9O_2$ and n-$C_5H_{11}O_2$ are reported to be comparable to that of n-$C_3H_7O_2$, and a factor of two to three lower than those for i-$C_4H_9O_2$ and neo-$C_5H_{11}O_2$ (see Table 9), suggesting that there may be sensitivity to whether the alkyl group is linear or branched. In the absence of additional data (and noting that the kinetics of neo-$C_5H_{11}O_2$ were the most directly determined of the set of C_4 and C_5 primary alkyl peroxy radicals), the above (stronger) size dependence is provisionally applied here.

Data for tertiary alkyl peroxy radicals are currently limited to t-$C_4H_9O_2$, and the corresponding rate coefficient is currently applied as the reference rate coefficient at 298 K, independent of radical size (see Fig. 3):

$$k^\circ_{RO2RO2(tert)} = 2.1 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \qquad (~~15~~16)$$

Fig. 3 also shows data for allylic and β-hydroxyalkyl RO_2, demonstrating that the presence of both these functionalities has an activating effect on self-reaction reactivity. The allylic peroxy radical category includes two δ-hydroxyallylic peroxy radicals, and the assumption is made here that the δ-hydroxy group is too remote to have an influence. Table 12 summarizes a series of activation factors (defined in terms of the parameters α and β) for allylic-, ~~benzyl~~β-aryl-, hydroxy-, alkoxy- and oxo- groups, optimized on the basis of the data in Tables 9 and 10. These are used in conjunction with the reference rate coefficients in Eq. (~~13~~14)-(~~15~~16), to calculate the self-reaction rate coefficient for a given peroxy radical at 298 K, k_{RO2RO2}, as follows:

$$k_{RO2RO2} = k^\circ_{RO2RO2} \times \alpha/(k^\circ_{RO2RO2})^{\beta} = \alpha \times (k^\circ_{RO2RO2})^{1-\beta} \qquad (~~16~~17)$$

Here, k°_{RO2RO2} represents the appropriate reference rate coefficient (i.e. for primary, secondary or tertiary RO_2, as appropriate) as defined by Eq. (~~13~~14)-(~~15~~16); and the term $\alpha/(k^\circ_{RO2RO2})^{\beta}$ describes the level of activation from the given substituent. The inclusion of k°_{RO2RO2} within this activation term is required because the relative enhancement of reactivity resulting from a given substituent appears to decrease as the reactivity increases, as illustrated for the β-hydroxyalkyl group data in Fig. 3. Based on this method, the estimated rate coefficients correlate well with those observed for the series of peroxy radicals for which data are currently available (summarized in Tables 9 and 10), as shown in Fig. 4. It is emphasized, however, that the parameters for several of the substituent groups are based on data for very limited sets of peroxy radicals, and additional data would be valuable to test and constrain the method.

Information on the effects of multiple substituents is limited to the data for the secondary and tertiary β-hydroxyallylic peroxy radicals, $HOCH_2CH(O_2)CH{=}CH_2$ and $HOCH_2C(CH_3)(O_2)C(CH_3){=}CH_2$, given in Table 10. The reported rate coefficients are consistent with the activating impacts of the β-hydroxy and allylic substituents being approximately cumulative, suggesting that an activation factor should be applied for each relevant organic substituent. However, this would lead to unreasonably large estimated values of k_{RO2RO2} for secondary and tertiary peroxy radicals containing two or three of the most activating substituents, such that the impact needs to be limited. In multifunctional peroxy radicals, therefore, an activating factor is only applied for the most activating oxygenated substituent in a given peroxy radical, with an additional factor also applied only for the specific cases of an allylic or a ~~benzyl~~ β-aryl substituent, again limited to one (i.e. the most activating) factor if the peroxy radical contains more than one allylic or ~~benzyl~~ β-aryl group. In these specific cases, therefore,

$$\alpha = (\alpha_1 \times \alpha_2) \qquad (18)$$

~~and~~

$$\beta = (\beta_1 + \beta_2) \qquad (19)$$

~~,~~ where α_1 and β_1 refer to the oxygenated substituent, and α_2 and β_2 refer to either the allylic substituent or the ~~benzyl~~ β-aryl substituent. Further information is required to allow the impacts of multiple substituents to be defined more rigorously.

2.6.2 Parameterized representation

The rate coefficients for cross-reactions of peroxy radicals (reaction (R8)) have often been inferred from those for the self-reactions of the participating peroxy radicals, using a geometric mean rule as first suggested by Madronich and Calvert (1990), i.e:

$$k_8 = 2 \times (k_7 \times k_{7'})^{0.5} \qquad (20)$$

where k_8 is the cross-reaction rate coefficient, and k_7 and $k_{7'}$ are the self-reaction rate coefficients for the participating peroxy radicals, RO_2 and $R'O_2$. Fig. 5 shows that such a correlation provides a reasonable guide in many cases (although a clear deviation from the rule occurs for the particular case of reactions involving acyl peroxy radicals). In the very simplified MCM approach, the rate coefficient for the single parameterized permutation reaction of a given peroxy radical (reaction (R9)) is based on that estimated for the cross-reaction of the peroxy radical with CH_3O_2. This is regarded as a logical choice, because CH_3O_2 is the most abundant organic peroxy radical in the atmosphere (and therefore most commonly the major reaction partner), and also possesses a self-reaction rate coefficient that is in the middle of the range of reported values (see Tables 9 and 10). Taking account of the correlations in Fig. 5, the rate coefficients (in cm^3 $molecule^{-1}$ s^{-1}) for the parameterized permutation reactions at 298 K are defined as follows:

For acyl RO_2: $k_{AP(298K)} = 1.1 \times 10^{-11}$ (~~17~~21)

For other RO_2 (except CH_3O_2): $k_{RO2(298K)} = f_{RO2} \times 2 \times (k_{RO2RO2} \times k_{298}(CH_3O_2{+}CH_3O_2))^{0.5}$ (~~18~~22)

Here, $k_{298}(CH_3O_2{+}CH_3O_2)$ is the rate coefficient for the self-reaction of CH_3O_2 at 298 K (= 3.5×10^{-13} cm^3 $molecule^{-1}$ s^{-1}) and k_{RO2RO2} is the 298 K self-reaction rate coefficient, estimated as described above (Sect. 2.6.1). f_{RO2} is a scaling factor that is introduced to describe systematic deviations from the geometric mean rule, if required. Based on the correlations in Fig. 5, a unity value of f_{RO2} is considered acceptable for primary and secondary peroxy radicals (i.e. no deviation from the geometric mean rule), whereas a value of f_{RO2} = 2 is applied to tertiary peroxy radicals. This elevated scaling factor is based on observation of Jenkin et al. (1998) for complex tertiary RO_2 cross reactions.

Based on the reported temperature dependences of peroxy radical self- and cross-reactions (see Tables 9 and 10, and Table 11 comments), k_{AP} and k_{RO2} are assigned respective pre-exponential factors of 2.0×10^{-12} and 1.0×10^{-13} cm^3 $molecule^{-1}$ s^{-1}. For acyl peroxy radicals, this is consistent with the temperature dependence reported for the reaction of $CH_3C(O)O_2$ with CH_3O_2, and results in the following temperature dependent expression in all cases:

$k_{AP} = 2.0 \times 10^{-12} \exp(508/T)$ cm^3 $molecule^{-1}$ s^{-1} (~~19~~23)

For k_{RO2}, the pre-exponential factor is a rounded value, based on the geometric mean of those for the self-reactions of non-acyl peroxy radicals given in Tables 9 and 10. This results in the following temperature dependence expression for non-acyl peroxy radicals (except CH_3O_2),

$k_{RO2} = 1.0 \times 10^{-13} \exp(-(E_{RO2}/R)/T)$ cm^3 $molecule^{-1}$ s^{-1} (~~20~~24)

with E_{RO2}/R having a case dependent value of $-298 \times \ln(k_{RO2(298\,K)}/10^{-13})$, where $k_{RO2(298\,K)}$ is defined by Eq. (~~18~~22). Examples of specific rate coefficients estimated using this method are given in Sect. S5, for the peroxy radicals formed from the sequential addition of OH and O_2 to isoprene. As indicated above, the collective rate of all the permutation reactions of a particular peroxy radical is then represented by a pseudo-unimolecular reaction (reaction (R9)), which has an assigned rate coefficient equal to $k_{AP} \times \sum[RO_2]$ for acyl peroxy radicals, and $k_{RO2} \times \sum[RO_2]$ for all other peroxy radicals (except CH_3O_2). For the specific case of CH_3O_2, the applied rate coefficient (k_{CH3O2}) is twice the self-reaction rate coefficient given in Table 9,

$k_{CH3O2} = 2.06 \times 10^{-13} \exp(365/T)$ cm^3 $molecule^{-1}$ s^{-1} (~~21~~25)

with the pseudo-unimolecular reaction rate coefficient equal to $k_{CH3O2} \times \sum[RO_2]$. This representation is therefore consistent with CH_3O_2 being lost via its self-reaction with the recommended rate coefficient when it is the dominant radical.

Each reaction potentially has up to four product channels, the branching ratios of which depend on the structure of the radical, as shown in Table 13:

$RO_2 \rightarrow RO$ (R9a)

$\rightarrow R_{-H}{=}O$ (R9b)

$\rightarrow ROH$ (R9c)

[$\rightarrow RO_{(peroxide)}$ (R9d)]

Channels (R9a)-(R9c) have been considered previously in the MCM (Jenkin et al., 1997; Saunders et al., 2003). They are the pseudo-unimolecular representation of the self-reaction channels (R7a) and (R7b) and the cross-reaction channels (R8a)-(R8c), which are reported to account for most of the reaction, particularly for smaller peroxy radicals (e.g. Lightfoot et al., 1992; Orlando and Tyndall, 2012). As shown in Table 13, channels (R9a)-(R9c) continue to represent the complete reaction in the current parameterized methodology.

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) ~~the pseudo-unimolecular approach~~ notionally represents the monomeric contribution the given peroxy radical makes to the total formation of (dimeric) peroxide products. However, ~~but~~ 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, ~~channel (R9d)~~it ~~can~~ 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.

3 Unimolecular reactions of RO_2 radicals

Unimolecular isomerization reactions are potentially available for some classes of RO_2. These generally fall into the category of either ring-closure reactions (where the peroxy radical adds intra-molecularly to an unsaturated linkage to form a peroxide-bridged radical product); or reactions involving the migration of a hydrogen atom to the peroxy radical group (e.g. forming a hydroperoxy-substituted organic radical product when abstraction from a C-H bond occurs). For some RO_2

structures, these reactions have been shown to compete with (or dominate over) the bimolecular reactions under some atmospheric conditions, as discussed further below in Sects. 3.1 and 3.2. Evidence for the operation of peroxy radical isomerization reactions has been reported in numerous theoretical and laboratory studies (e.g. Vereecken and Peeters, 2004; Peeters et al., 2009; 2014; Crounse et al., 2013; Ehn et al., 2014; 2017; Jokinen et al., 2014; Rissanen et al., 2015; Jørgensen et al., 2016; Praske et al., 2017; 2019; Otkjær et al., 2018; Mohammed et al., 2018), and new information is constantly emerging on this important aspect of peroxy radical chemistry (e.g. Biachi et al., 2019; Xu et al., 2019; Møller et al., 2019). The present section provides a summary of selected classes of isomerization reaction that are currently being considered and represented in ongoing mechanism development work. However, it does not currently attempt to provide a full treatment of unimolecular reactions of RO_2 radicals, which will be considered further in future work as more new information becomes available.

3.1 Ring-closure reactions of RO_2

Table 14 shows ~~the~~ representative rate coefficients ~~assigned to~~for selected template ring-closure reactions. The first entry relates to the β-hydroxy cyclohexadienylperoxy radicals formed from the addition of O_2 to OH-aromatic hydrocarbon adducts. As discussed in the companion paper on the OH-initiated oxidation of aromatic VOCs (Jenkin et al., 2018b), these peroxy radicals are represented to undergo rapid and exclusive ring closure to produce a hydroxy-dioxa-bicyclo or "peroxide-bicyclic" radical. This reaction has been calculated to dominate over alternative bimolecular reactions of the peroxy radicals under atmospheric conditions (see Table 14), although evidence for competitive loss via bimolecular reactions has been characterized in experimental studies using high concentrations of NO and/or RO_2 (e.g. Birdsall et al., 2010; Birdsall and Elrod, 2011).

The remaining reactions in Table 14 are based on information presented by Vereecken and Peeters (2004) for specific peroxy radicals formed from the sequential addition of OH and O_2 to isoprene, α-pinene and β-pinene. That information has been used to assign or infer representative rate coefficients to the series of related template peroxy radical structures presented in Table 14. In these cases, the reactions are expected to occur at rates that can compete to varying extents with loss via bimolecular reactions (or other unimolecular reactions discussed below) under atmospheric conditions. 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.

3.2 Hydrogen atom migration reactions of RO_2

Table 15 shows selected hydrogen atom migration reactions that are currently considered. The rate coefficient assigned generally to the 1,4 formyl H-shift reaction of α-formyl peroxy radicals is based on that determined for the methacrolein-derived peroxy radical, $HOCH_2C(CH_3)(O_2)C(=O)H$, in the experimental study of Crounse et al. (2012). It is noted that this is slightly higher than, but comparable with, the range of values reported for α-formyl peroxy radicals in the preliminary calculations of Peeters and Nguyen (2012).

The rate coefficients assigned to the 1,4 hydroxyl H-shift reactions of (thermalized) α-hydroxy peroxy radicals are based on those estimated for secondary, tertiary and cyclic peroxy radicals in the theoretical study of Hermans et al. (2005). As discussed in the companion paper on the OH-initiated oxidation of aliphatic VOCs (Jenkin et al., 2018a), thermalized α-hydroxy peroxy radicals are represented to be increasingly formed from the reactions of O_2 with larger α-hydroxy organic radicals (i.e. those with $n_{\mathrm{CON}} > 5$). At the assigned rates, the 1,4 hydroxyl H-shift reaction is likely to be the major fate of the majority of thermalized α-hydroxy peroxy radicals under atmospheric conditions, and therefore indistinguishable from that of the chemically activated α-hydroxy peroxy radical adducts that are formed predominantly from the reactions of O_2 with small α-hydroxy organic radicals (see Sect. 6.2 of Jenkin et al., 2018a). However, the rates of the 1,4 hydroxyl H-shift reactions are formalized in the present work, to allow for the representation of competing rapid isomerization reactions for specific structurally-complex peroxy radicals (e.g. the 1,6 enol H-shift reaction discussed below), or with bimolecular reactions under appropriate conditions. It is noted that evidence for competitive loss via bimolecular reactions has been characterized in experimental studies using high concentrations of NO (e.g. Orlando et al., 2000; Jenkin et al., 2005; Aschmann et al., 2010), leading to the formation of organic acids.

The remaining reactions in Table 15 are inferred from information reported for specific unsaturated peroxy radicals formed during the OH-initiated oxidation of isoprene, taking particular account of the work of Peeters et al. (2009; 2014) on the Leuven isoprene mechanism (LIM1), which has been largely verified by experimental study (e.g. Wennberg et al., 2018; and references therein). The rate coefficients for the 1,5 hydroxyl H-shift reactions are those reported by Peeters et al. (2014) for the corresponding unsaturated secondary and tertiary β-hydroxy peroxy radicals formed from the sequential addition of OH and O_2 to isoprene, with these also being generally consistent with those reported by da Silva et al. (2010). 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 rate coefficient for the rapid 1,6 enol H-shift reaction is the geometric mean of those calculated for (*Z*)-$HOCH=C(CH_3)CH(O_2)CH_2OH$ and (*Z*)-$HOCH=CHC(CH_3)(O_2)CH_2OH$ by Peeters and Nguyen (2012). Once again, the 1,6 enol H-shift reaction is likely to be the major fate of the majority of peroxy radicals containing the relevant sub-structure (see Table 15) under atmospheric conditions, but the rate is formalized in the present work, to allow for the representation of competing rapid isomerization reactions for specific structurally-complex peroxy radicals, e.g. the 1,4 hydroxyl H-shift reaction discussed above, or other reactions that may be considered and represented in future work.

As indicated above, the present paper does not attempt to provide a full treatment of unimolecular reactions of RO_2 radicals, which ideally 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 ~~some~~ a number of model systems (e.g. Crounse et al., 2013; Jørgensen et al., 2016; Praske et al., 2017; Otkjær et al., 2018). Such~~, and further~~ studies ~~of this type would help to~~provide the basis for ~~define~~ defining systematic structure-activity methods for a wide~~r~~ range of RO_2 radicals and their potential isomerization reactions, and are being considered in ongoing work. A further consideration, highlighted in those studies, is that the rates of the reverse isomerization reactions are sometimes sufficiently rapid that the product radical may not be fully trapped by onward reaction (e.g. addition of O_2) under atmospheric conditions. It is noted that the explicit representation of a very large number of rapid reversible reactions in detailed mechanisms can have implications for computational efficiency, and needs to be considered carefully in method development and implementation.

4 Conclusions

Published kinetics and branching ratio data have been reviewed for the bimolecular reactions of organic peroxy radicals (RO_2), with information for selected unimolecular isomerization reactions also summarized and discussed. The information has been used to define generic rate coefficients and structure-activity relationship (SAR) methods for the reactions of a series of important classes of hydrocarbon and oxygenated RO_2 radical, for application in the next generation of explicit detailed chemical mechanisms, based on GECKO-A and the MCM.

The availability of kinetic and mechanistic data for peroxy radical reactions has increased substantially since the appraisals of Saunders et al. (2003) and Aumont et al. (2005), on which the previous treatments of peroxy radical chemistry in the MCM and GECKO-A were mainly based. These advances have allowed improved and updated methods to be defined and summarized in the present work for an extended set of peroxy radical reactions. Nevertheless, there are still a number of specific areas (commented on in Sects. 2 and 3) where information is lacking and further studies would be beneficial. These include the following:

- Kinetics studies of the reactions with NO have only been reported for a limited number of acyl peroxy radicals. Further studies, particularly for larger and highly-oxygenated acyl peroxy radicals, would help to establish whether size and/or the presence of additional substituent groups has an effect on reactivity.
- 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.
- For the reactions with NO_3, studies for ≥ C_2 (non-acyl) RO_2 are dominated by primary peroxy radicals. Further studies are therefore required for secondary and tertiary radicals, and product information is generally required for a variety of peroxy radical classes to test assumption that the reaction proceeds via a single channel forming RO, NO_2 and O_2.

- The reactions of ≥ C_2 hydrocarbon RO_2 with OH are believed to produce a thermalized hydrotrioxide, ROOOH, as the major product. Detailed experimental and theoretical studies are therefore required to establish the atmospheric fate of these ROOOH species. Studies of the reactions of oxygenated RO_2 with OH are also required.
- The reactions of HO_2 with several oxygenated RO_2 classes have been shown to proceed via multiple channels, although the temperature-dependences of the product channels have generally not been studied. Additional studies of their temperature dependences would therefore be valuable, in addition to information for larger sets of oxygenated RO_2 within some classes. Kinetics studies have only been reported for a limited number of acyl peroxy radicals. Further studies, particularly for larger and highly-oxygenated acyl peroxy radicals, would help to establish whether size and/or the presence of additional substituent groups has an effect on reactivity.
- For the self- and cross-reactions of peroxy radicals, further information is required to allow the impacts of multiple substituents on the kinetics to be defined more rigorously. Further systematic studies of the formation of ROOR + O_2 (from the self-reaction of RO_2) and ROOR' + O_2 (from the cross-reaction of RO_2 with $R'O_2$) are also required as a function of peroxy radical size and functional group content.
- For unimolecular isomerization reactions, further systematic studies are required of the rates of 1,*n* H-shift reactions from C-H and O-H bonds in different chemical environments, and of the effect of ring size and substituents on ring-closure reactions, to build upon recently reported data for these reaction classes.

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Author contributions. All authors defined the scope of the work. MEJ developed and revised the estimation methods and drafted the manuscript, which were reviewed and refined by all authors.

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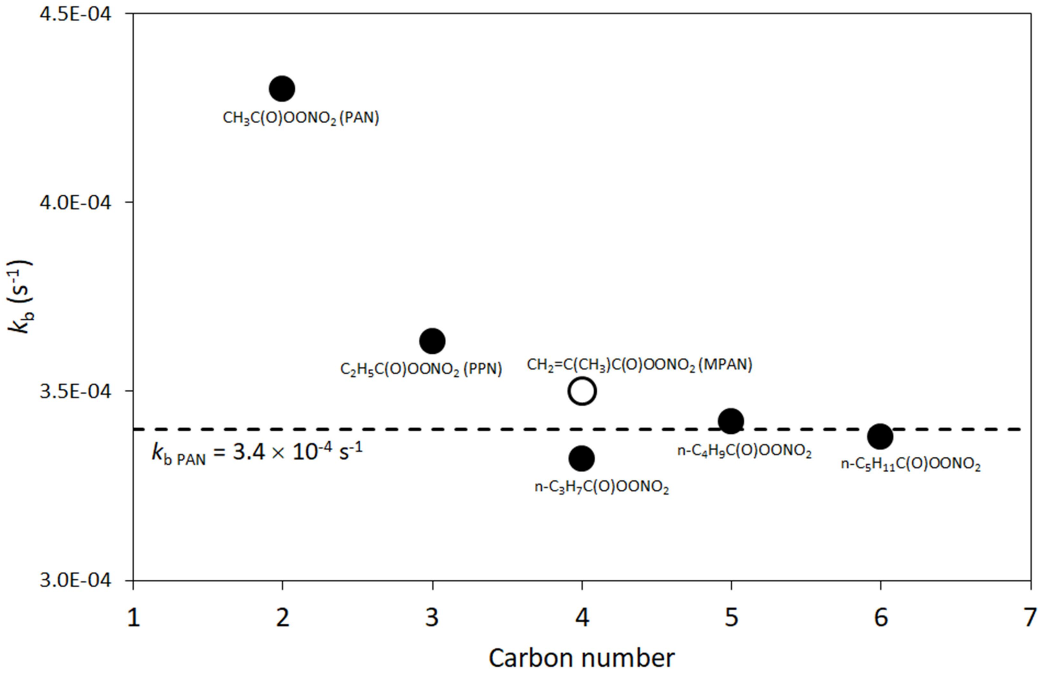


Figure 1: Reported thermal decomposition rates of selected peroxyacyl nitrates at 298 K and 760 Torr. Values for PAN, PPN and MPAN are the IUPAC Task Group recommendations (http://iupac.pole-ether.fr/). The other values are taken from the systematic study of Kabir et al. (2014), which also reports consistent values for PAN and PPN. The broken line is the generic rate coefficient, $k_{b\ PAN}$, for the decomposition of $RC(O)OONO_2$ structures (see Sect. 2.2 and Table 4).

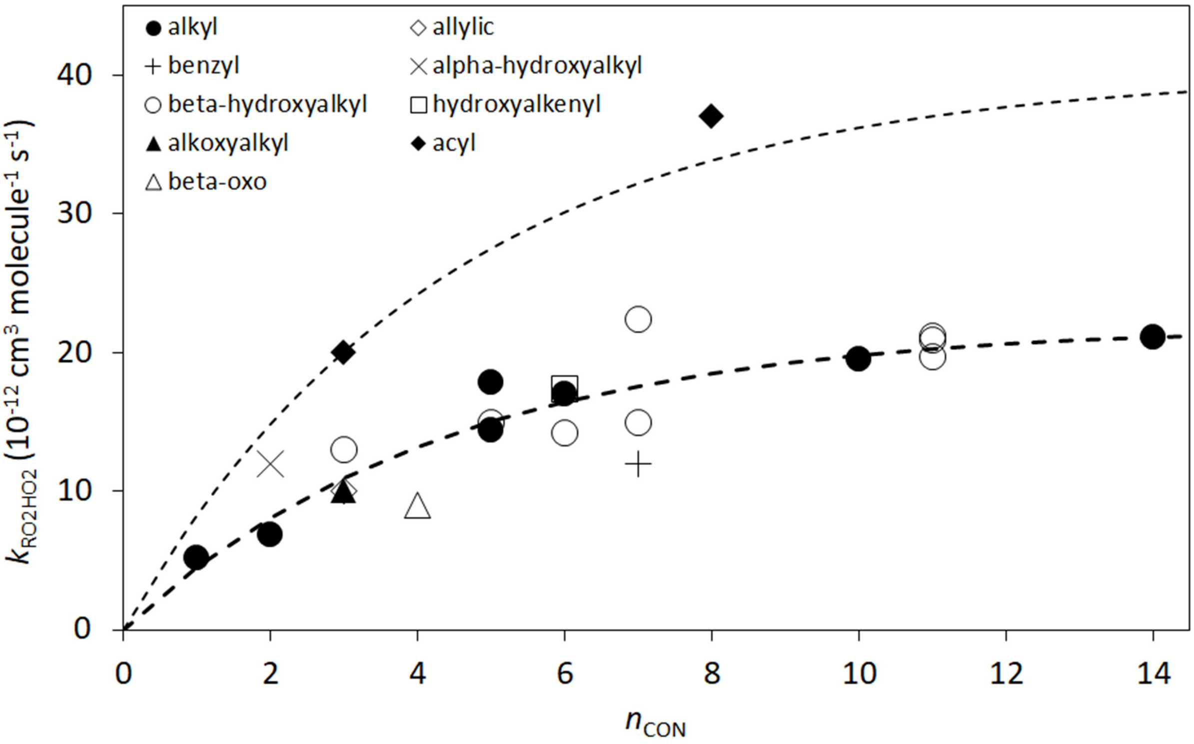


Figure 2: Rate coefficients for the reactions of various classes of RO_2 radicals with HO_2 as a function of n_{CON} at 298 K. The heavy broken line is the best fit to the data for alkyl and β-hydroxyalkyl RO_2 on the basis of the assumed function $k = A(1-\exp(B.n_{CON}))$. The light broken line is the same function with the 298 K value of ~~*A*~~ *k* increased by a factor of ~~two~~ 1.83 (see Sect. 2.5).

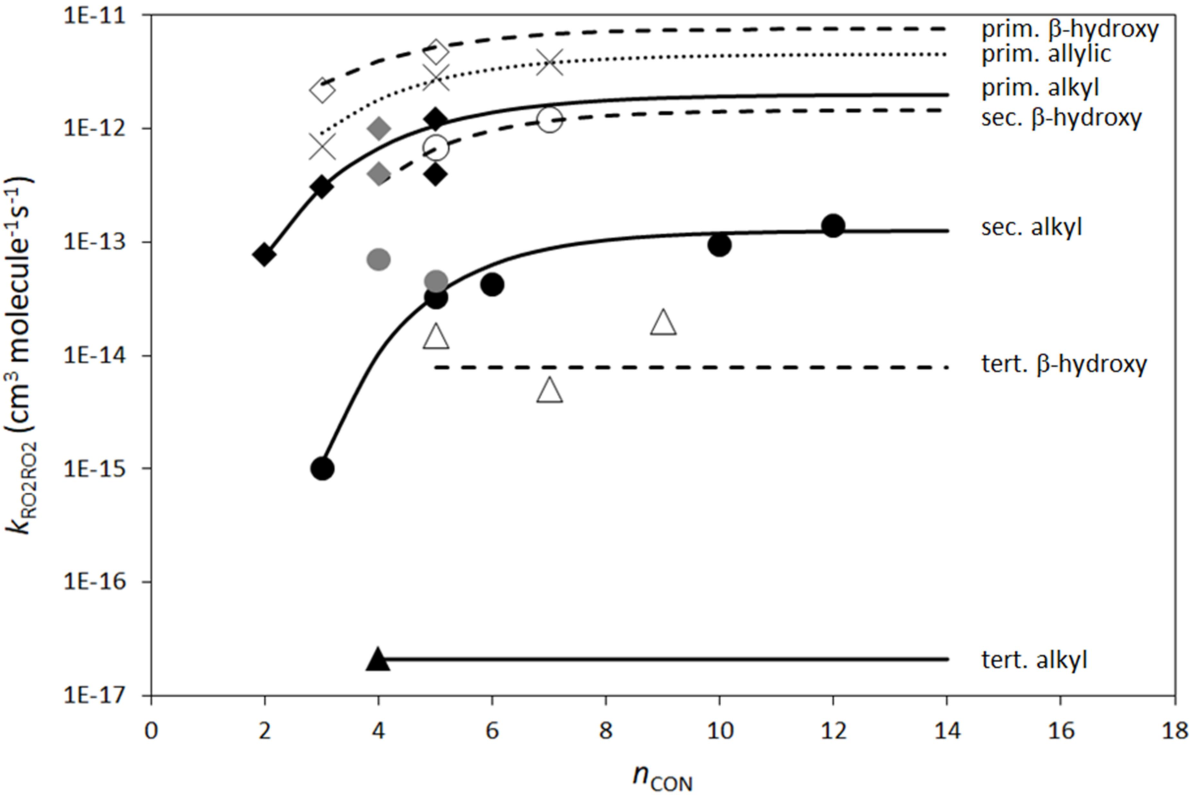


Figure 3: Rate coefficients for the self-reactions of alkyl (filled points), β-hydroxyalkyl (open points) and allylic (×) RO_2 at 298 K as a function of n_{CON}. Grey filled points indicate where the reported rate coefficient has not been corrected for secondary chemistry. Where available, data are shown for primary, secondary and tertiary radicals containing the given functionalities. Primary, secondary and tertiary alkyl and β-hydroxyalkyl radicals are shown as diamonds, circles and triangles, respectively. The "allylic" peroxy radical group contains only primary radicals and includes "δ-hydroxyallylic" peroxy radicals. The lines represent the calculated rate coefficients fitted to the data using the methods described in Sect. 2.6.

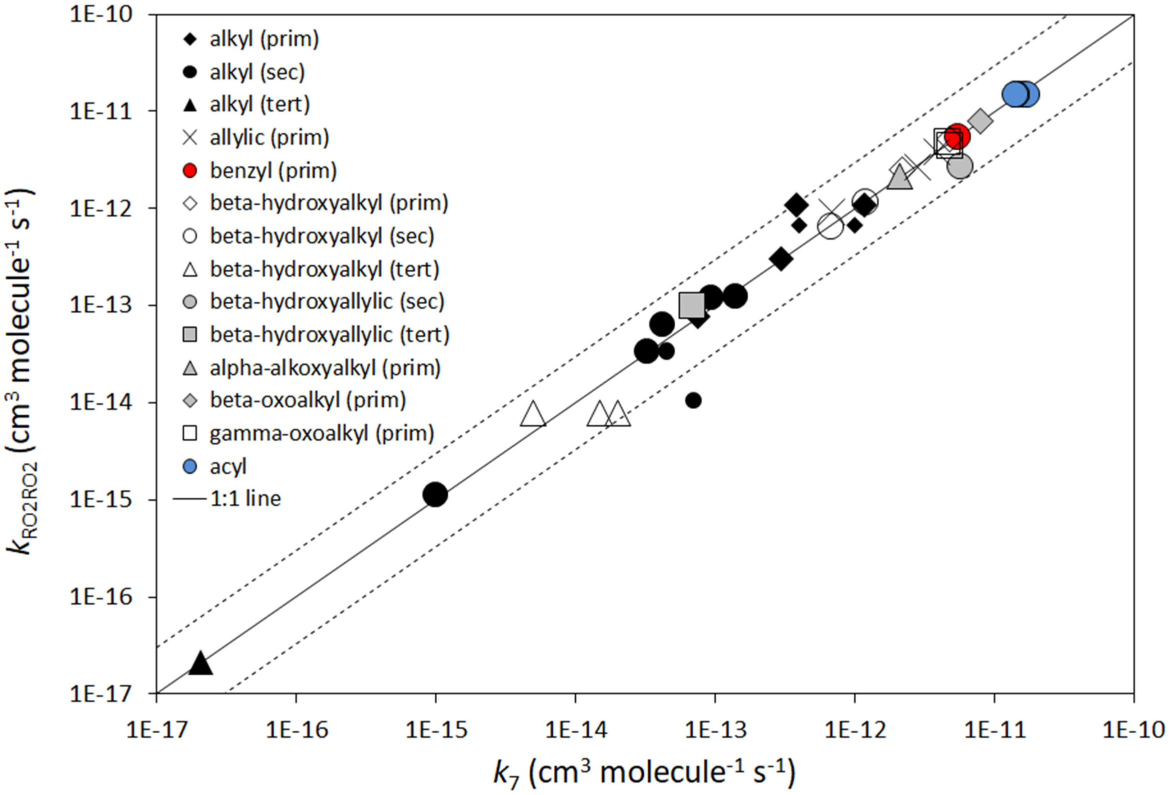


Figure 4: Scatter plot of estimated rate coefficients (k_{RO2RO2}) for peroxy radical self-reactions with those reported (k_7), as listed in Tables 9 and 10. Those shown with reduced size symbols are where the reported value of k_7 was not corrected for secondary chemistry (see Table 9 comments). The broken lines show the factor of 3 range. 5

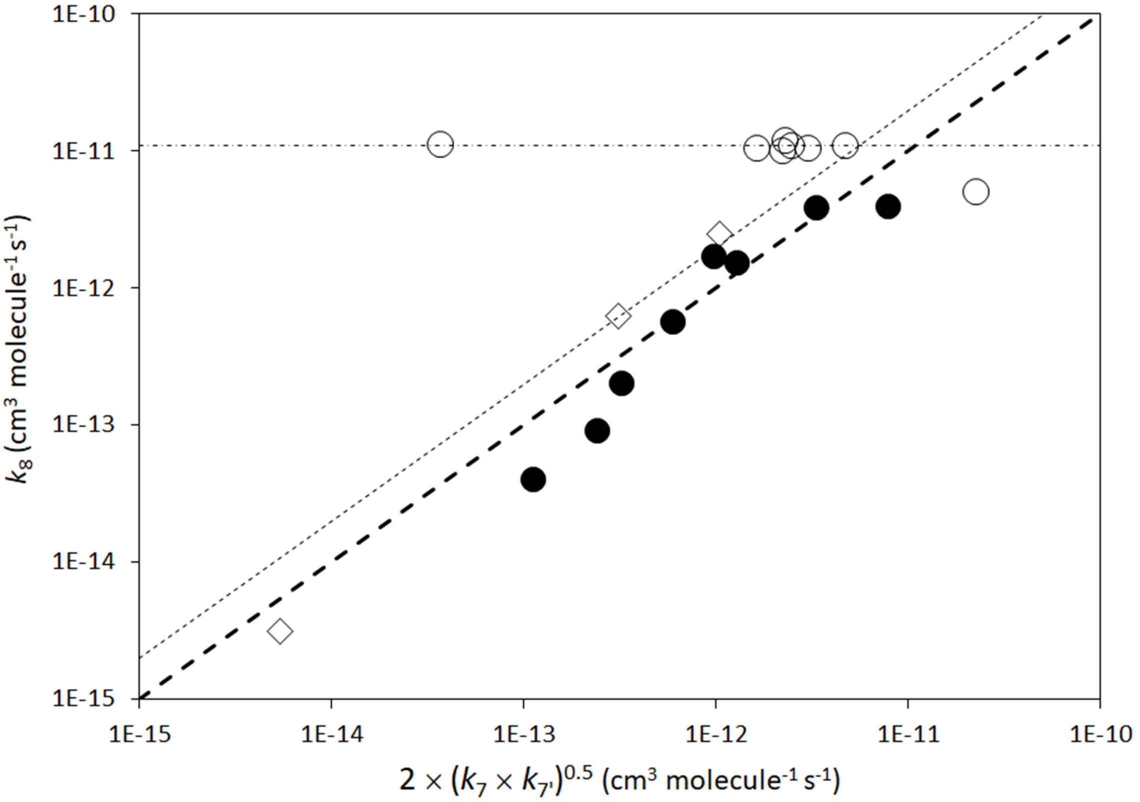


Figure 5: Scatter plot of rate coefficients for peroxy radical cross-reactions (k_8) with the geometric mean of the self-reaction rate coefficients (denoted k_7 and $k_{7'}$) for the participating peroxy radicals, RO_2 and $R'O_2$. Open circles are reactions involving an acyl peroxy radical and a non-acyl peroxy radical; closed circles are reactions involving combinations of primary and secondary peroxy radicals; open diamonds are reactions involving a tertiary peroxy radical and a primary or secondary peroxy radical. The heavy broken line is a 1:1 relationship; the light broken line is a 2:1 relationship; the dot-dash line is $k_8 = 1.1 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}.

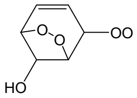
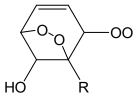
Table 1. Kinetic data for the reactions of hydrocarbon and oxygenated peroxy radicals with NO. Where available, the temperature dependence is given by $k = A.\exp(-E/RT)$.

Peroxy radical	A	E/R	$k_{298\ K}$	Comment
	(10^{-12} cm^3 molecule^{-1} s^{-1})	(K)	(10^{-12} cm^3 molecule^{-1} s^{-1})	
Alkyl and cycloalkyl				
CH_3O_2	2.30	-360	7.7	(a)
$C_2H_5O_2$	2.55	-380	9.1	(a)
n-$C_3H_7O_2$	2.90	-350	9.4	(a),(b)
i-$C_3H_7O_2$	2.70	-360	9.0	(a),(b)
t-$C_4H_9O_2$			8.3	(a)
2-$C_5H_{11}O_2$			8.0	(b)
c-$C_5H_9O_2$			10.9	(b)
Allylic (alk-2-enyl)				
$CH_2=CHCH_2O_2$			10.5	(b)
β-Hydroxyalkyl				
$HOCH_2CH_2O_2$			8.7	(c)
propene-derived			9.5	(c),(d)
but-1-ene-derived			9.6	(c),(e)
$CH_3CH(OH)CH(O_2)CH_3$			9.4	(c)
methylpropene-derived			9.6	(c),(f)
Hydroxyalkenyl				
buta-1,3-diene derived			8.8	(c),(g)
isoprene-derived			8.8	(a),(c),(h)
Oxoalkyl				
$CH_3C(O)CH_2O_2$			8.0	(a),(i)
Hydroxy-oxyalkyl				
methacrolein-derived			9.3	(j),(k)
methylvinyl ketone-derived			8.4	(j),(l)
Hydroxy-dioxa-bicyclo				
1,3,5-trimethylbenzene-derived			7.7	(m)
Acyl				
$CH_3C(O)O_2$	7.5	-290	20	(a)
$C_2H_5C(O)O_2$	6.7	-340	21	(a)
$CH_2=CH(CH_3)C(O)O_2$	8.7	-290	23	(n)
~~CH~~$C(O)(OOH)CH_2CH_2CH_2CH(OOH)C(O)O_2$			34	(o)

Comments

[a] IUPAC Task Group recommendation (http://iupac.pole-ether.fr/); [b] Based on Eberhard and Howard (1996; 1997), Eberhard et al. (1996); [c] Based on Miller et al. (2004); [d] Mixture of $CH_2(OH)CH(O_2)CH_3$ and $CH_2(O_2)CH(OH)CH_3$; [e] Mixture of $CH_2(OH)CH(O_2)C_2H_5$ and $CH_2(O_2)CH(OH)C_2H_5$; [f] Mixture of $CH_2(OH)C(O_2)(CH_3)_2$ and $CH_2(O_2)C(OH)(CH_3)_2$; [g] Mixture of $CH_2(OH)CH(O_2)CH=CH_2$, $CH_2(OH)CH=CHCH_2O_2$ and $CH_2(O_2)CH(OH)CH=CH_2$; [h] Mixture of $CH_2(OH)C(O_2)(CH_3)CH=CH_2$, $CH_2(OH)C(CH_3)=CHCH_2O_2$, $CH_2(O_2)C(CH_3)(OH)CH=CH_2$, $CH_2(OH)CH(O_2)C(CH_3)=CH_2$, $CH_2(OH)CH=C(CH_3)CH_2O_2$ and $CH_2(O_2)CH(OH)C(CH_3)=CH_2$; [i] Based on Sehested et al. (1998); [j] Based on Hsin and Elrod (2007); [k] Mixture of $CH_2(OH)C(O_2)(CH_3)CHO$ and $CH_2(O_2)C(OH)(CH_3)CHO$; [l] Mixture of $CH_2(OH)CH(O_2)C(=O)CH_3$ and $CH_2(O_2)CH(OH)C(=O)CH_3$; [m] Elrod (2011). Mixture of two complex radicals of molecular formula $HOC_9H_{12}[OO]O_2$, although with one isomer likely dominant; [n] de Gouw and Howard (1997); [o] Berndt et al. (2015). Inferred to be the complex oxo-di-hydroperoxy acyl peroxy radical shown, on the basis of its molecular mass and a proposed mechanism.

Table 2. Values of the scaling factor, f_a, applied to the branching ratio calculation for the reaction of RO_2 with NO.

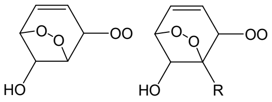
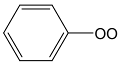
Class	substitution	f_a	Comment
default	primary	0.65	(a)
	secondary	1.0	
	tertiary	1.0	
	secondary	1.0	(b)
	tertiary	0.13	
	secondary	0.43	(b)
	tertiary	0.06	

Comments

[a] Applied in all cases, except for those covered by comment (b). f_a = 1 for secondary peroxy radicals, by definition. The equivalent value for tertiary peroxy radicals, and the lower value for primary peroxy radicals, are based on a consensus of information from Cassanelli et al. (2007), Orlando and Tyndall (2012) and Teng et al. (2015) and on previous consideration of the OH + isoprene system (Jenkin et al., 2015);

[b] Inhibition of nitrate formation has been reported for complex hydroxy-dioxa-bicyclo peroxy radicals derived from aromatics, relative to comparably sized alkyl peroxy radicals, by Rickard et al. (2010) and Elrod (2011), with a particular impact from the presence of alkyl substituents reported by Elrod (2011). The reduced values of f_a for tertiary peroxy radicals, and the general reduction in f_a for peroxy radicals with a neighbouring alkyl substituent (as shown), is inferred from the trend in nitrate yields reported for benzene, toluene, *p*-xylene and 1,3,5-trimethylbenzene by Elrod (2011).

Table 3. Values of the scaling factor, f_b, applied to the branching ratio calculation for the reaction of RO_2 with NO [a].

Class	f_b	Comment
$C_nH_{2n+1}OO$ (alkyl peroxy)	1.0	(b)
OO-C-C(OH)< , OO-C-C(OR)< , OO-C(OH)< , OO-C(OR)< , $\mathrm{OO\text{-}C\text{-}C(ONO_2)}$< ,OO-C-C(OOH)<	0.65	(c)
δ-hydroxy peroxy	0.8	(d)
OO-C-C(=O)-, OO-C-C(=O)-O-	0.3	(e)
OO-C(=O)-, OO-C-O-C(=O)-	0.0	(e),(f)
	0.33	(g)
	0.0	(h)

Comments

[a] A value of f_b needs to be applied to account for the effect of each relevant substituent (see Appendix 1 for further information); [b] f_b = 1 for alkyl peroxy radicals, by definition, and also used as a default in all cases other than those covered by comments (c)-(g); [c] 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). OO-C-C(OOH)< assumed to be in this category by analogy; [d] Based on the relative impacts of β-OH and δ-OH substituents reported by Yeh and Ziemann (2014a) and previous consideration of the OH + isoprene system (Jenkin et al., 2015); [e] f_b value for OO-C-C(=O)- informed by reported studies of ketone oxidation (Lightfoot et al., 1992; Praske et al., 2015); f_b values for OO-C-C(=O)-O- and OO-C-O-C(=O)- informed by reported studies of ester and dibasic ester oxidation (Tuazon et al., 1998b; 1999; Cavalli et al., 2001; Picquet-Varrault et al., 2001; 2002; Pimentel et al., 2010); [f] f_b = 0 for OO-C(=O)- is based on the general lack of observation of acyl nitrate products in systems where acyl peroxy radicals are formed; [g] Value set to recreate the hydroxy-dioxa-bicyclo nitrate yield reported for benzene by Elrod (2011); In conjunction with the values of f_a in Table 2, this also allows a consistent representation of the yields in the toluene, *p*-xylene and 1,3,5-trimethylbenzene systems (Elrod, 2011; Rickard et al., 2010); [h] f_b = 0 for phenyl (and other aryl) peroxy radicals is based on the general lack of observation of ~~phenyl~~ aryl nitrate products during the oxidation of aromatic hydrocarbons.

Table 4. Rate coefficients for the reactions of hydrocarbon and oxygenated RO_2 radicals with NO_2 and for the reverse decomposition of the RO_2NO_2 products. Generic rate coefficients for specified RO_2 classes are shown in bold font.

Peroxy radical	k_0	k_∞	F_c	$k_{298\ \mathrm{K},\ 760\ \mathrm{Torr}}$	Comment
Forward reaction, k_f (cm^3 molecule^{-1} s^{-1})					
CH_3O_2	1.2×10^{-30} (T/300)$^{-6.9}$ [M]	1.8×10^{-11}	0.36	4.2×10^{-12}	(a),(b)
$C_2H_5O_2$	1.3×10^{-29} (T/300)$^{-6.2}$ [M]	8.8×10^{-12}	0.31	5.1×10^{-12}	(a),(c)
n- and *sec*- $C_4H_9O_2$	-	9.6×10^{-12}	-	9.6×10^{-12}	(d)
RO_2	-	**9.0×10^{-12} (= $k_{f\ PN}$)**	-	**9.0×10^{-12}**	(e)
$CH_3C(O)O_2$	3.28×10^{-28} (T/300)$^{-6.87}$ [M]	1.125×10^{-11} (T/300)$^{-1.105}$	0.3	8.9×10^{-12}	(a),(c)
$C_2H_5C(O)O_2$	1.05×10^{-27} (T/300)$^{-6.87}$ [M]	1.125×10^{-11} (T/300)$^{-1.105}$	0.36	8.9×10^{-12}	(a),(f)
$RC(O)O_2$, $ROC(O)O_2$	-	**1.125×10^{-11} (T/300)$^{-1.105}$ (= $k_{f\ PAN}$)**	-	**1.1×10^{-11}**	(e),(g)
Reverse reaction, k_b (s^{-1})					
CH_3O_2	9.0×10^{-5} exp(-9690/T) [M]	1.1×10^{16} exp(-10560/T)	0.36	1.5	(a),(c)
$C_2H_5O_2$	4.8×10^{-4} exp(-9285/T) [M]	8.8×10^{15} exp(-10440/T)	0.31	3.4	(a),(c)
n- and *sec*- $C_4H_9O_2$	-	8.3×10^{15} exp(-10368/T)	-	6.4	(h)
$C_6H_{13}O_2$ isomers	-	7.5×10^{15} exp(-10368/T)	-	5.8	(h)
$C_8H_{17}O_2$ isomers	-	4.8×10^{15} exp(-10368/T)	-	3.7	(h)
RO_2	-	**7.6×10^{15} exp(-10400/T) (= $k_{b\ PN}$)**		**5.3**	(e),(i)
$CH_3C(O)O_2$	1.1×10^{-5} exp(-10100/T) [M]	1.9×10^{17} exp(-14100/T)	0.3	4.3×10^{-4}	(a),(c)
$C_2H_5C(O)O_2$	1.7×10^{-3} exp(-11280/T) [M]	8.3×10^{16} exp(-13940/T)	0.36	3.6×10^{-4}	(a),(c)
$CH_2{=}C(CH_3)C(O)O_2$	-	1.6×10^{16} exp(-13500/T)	-	3.5×10^{-4}	(c),(j)
$RC(O)O_2$	-	**5.2×10^{16} exp(-13850/T) (= $k_{b\ PAN}$)**	-	**3.4×10^{-4}**	(e),(k)
$ROC(O)O_2$	-	**$2 \times k_{b\ PAN}$**	-	**6.8×10^{-4}**	(e),(l)

Comments: [a] Rate coefficient for a pressure-dependent reaction is calculated using the expression: $k = F.k_0.k_\infty/(k_0 + k_\infty)$, where $\log_{10}F = \log_{10}(F_c)/(1+[\log_{10}(k_0/k_\infty)/N]^2)$ and $N = [0.75 - 1.27 \log_{10}(F_c)]$ (see http://iupac.pole-ether.fr/); [b] Based on the evaluation of Golden (2005); [c] Recommended by the IUPAC Task Group (http://iupac.pole-ether.fr/); [d] Reported by McKee et al. (2016) for a mixture of *n*-$C_4H_9O_2$ and *sec*-$C_4H_9O_2$ formed from reaction of Cl with butane; [e] Pressure-independent generic rate coefficient; [f] k_∞ assumed equivalent to that for $CH_3C(O)O_2 + NO_2$ reaction. k_0 scaled relative to that for $CH_3C(O)O_2$ to preserve the $C_2H_5C(O)O_2 + NO_2 \rightleftharpoons C_2H_5C(O)OONO_2$ equilibrium constant, k_f/k_b, over the pressure range 100-760 Torr. F_c is equivalent to that recommended for k_b; [g] Forward reaction rate coefficient, $k_{f\ PAN}$, is based on k_∞ for the $CH_3C(O)O_2 + NO_2$ reaction; [h] Based on Zabel et al. (1989), as recommended by Lightfoot et al. (1992), for isomeric mixtures formed from reactions of Cl with butane, hexane or octane. Assumed to be at high pressure limit at 800 Torr; [i] $k_{b\ PN}$ is rounded average of the reported rate coefficients for C_2-C_8 alkyl peroxy radicals; [j] Based on Roberts and Bertman (1992). Assumed to be at high pressure limit at 760 Torr; [k] $k_{b\ PAN}$, is based on a value of 3.4×10^{-4} s^{-1} at 298 K, which is the average of those reported for *n*-$C_3H_7C(O)OONO_2$, *n*-$C_4H_9C(O)OONO_2$ and *n*-$C_5H_{11}C(O)OONO_2$ (Kabir et al, 2014) and $CH_2{=}C(CH_3)C(O)O_2$ (Roberts and Bertman, 1992) (see Fig. 1). E/R is based on the average of the high pressure limit values for $CH_3C(O)O_2NO_2$, $C_2H_5C(O)O_2NO_2$ and $CH_2{=}C(CH_3)C(O)O_2$, and also consistent with the approximate value for *n*-$C_5H_{11}C(O)OONO_2$ (Kabir et al., 2014); [l] Pressure-independent generic rate coefficient for thermal decomposition of $ROC(O)O_2$ is a factor of two greater, based on data for $CH_3OC(O)O_2$ and $C_6H_5OC(O)O_2$ (Kirchner et al., 1999), with reduced thermal stability also consistent with data for $C_2H_5OC(O)O_2$ (Bossolasco et al., 2011).

Table 5. Kinetic data for the reactions of alkyl and oxygenated peroxy radicals with NO_3. Where available, the temperature dependence is given by $k = A.\exp(-E/RT)$.

Peroxy radical	A	E/R	$k_{298\ K}$	Comment
	(10^{-12} cm^3 molecule^{-1} s^{-1})	(K)	(10^{-12} cm^3 molecule^{-1} s^{-1})	
Alkyl and cycloalkyl				
CH_3O_2			1.2	(a)
$C_2H_5O_2$	8.9	390	2.4	(b)
c-$C_5H_9O_2$			~1.2	(c)
c-$C_6H_{11}O_2$			1.9	(c)
β-Hydroxyalkyl				
$(CH_3)_2C(OH)CH_2O_2$	16	480	3.2	(d)
Alkoxyalkyl				
$CH_3OCH_2O_2$	13.6	435	3.2	(d)
Oxoalkyl				
$CH_3C(O)CH_2O_2$	5.47	282	2.1	(d)
Acyl				
$CH_3C(O)O_2$			3.2	(e)

Comments

[a] IUPAC Task Group recommendation (http://iupac.pole-ether.fr/); [b] $k_{298\ K}$ based on an average of the values reported by Biggs et al. (1995), Ray et al. (1996), Vaughan et al. (2006) and Laversin et al. (2016). E/R taken from Laversin et al. (2016); [c] Taken from Vaughan et al. (2006); [d] Taken from Kalalian et al. (2018) ; [e] Taken from Doussin et al. (2003). Canosa-Mas et al. (1996) reported a comparable value of $k = (4.0 \pm 1.0) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} over the range 403-443 K.

Table 6. Kinetic data for the reactions of peroxy radicals with OH. Where available, the temperature dependence is given by $k = A.\exp(-E/RT)$.

Peroxy radical	A	E/R	$k_{298\ K}$	Comment
	(10^{-11} cm^3 molecule^{-1} s^{-1})	(K)	(10^{-10} cm^3 molecule^{-1} s^{-1})	
CH_3O_2	3.7	-350	1.2	(a)
$C_2H_5O_2$			1.2	(b)
(n- and i-) $C_3H_7O_2$			1.4	(c)
(n- and sec-) $C_4H_9O_2$			1.5	(c)

Comments

[a] IUPAC Task Group recommendation (http://iupac.pole-ether.fr/) based on Assaf et al. (2016) and Yan et al. (2016), with an uncertainty of a factor of two assigned to k_{298K}; [b] IUPAC Task Group recommendation (http://iupac.pole-ether.fr/) based on Faragó et al. (2015), with an uncertainty of a factor of 1.6 assigned to k_{298K}. A consistent value of $k_{298\ K} = (1.3 \pm 0.3) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} has more recently been reported by Assaf et al. (2017b); [c] Global rate coefficients, $k_{298\ K} = (1.4 \pm 0.3) \times 10^{-10}$ and $(1.5 \pm 0.3) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, reported by Assaf et al. (2017b) for isomeric mixtures of peroxy radicals formed from reactions of Cl atoms with propane and butane, respectively.

Table 7. Kinetic data for the reactions of hydrocarbon and oxygenated peroxy radicals with HO_2. Where available, the temperature dependence is given by $k = A.\exp(-E/RT)$.

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})	
Alkyl and cycloalkyl				
CH_3O_2	3.8	-780	5.2	(a)
$C_2H_5O_2$	6.4	-710	6.9	(a)
neo-$C_5H_{11}O_2$	1.4	-1380	14.4	(b)
c-$C_5H_9O_2$	2.1	-1323	17.8	(b)
c-$C_6H_{11}O_2$	2.6	-1245	17.0	(b)
decane-derived			19.5	(c),(d)
tetradecane-derived			21.1	(c),(e)
Allylic (alk-2-enyl)				
CH_2=$CHCH_2O_2$	~10	-700	~10	(f)
~~Benzyl~~β-aryl				
$C_6H_5CH_2O_2$	1.5	-1310	12.0	(a)
α-Hydroxyalkyl				
$HOCH_2O_2$	0.056	-2300	12.0	(a)
β-Hydroxyalkyl				
$HOCH_2CH_2O_2$			13.0	(a)
$CH_3CH(OH)CH(O_2)CH_3$			15.0	(a),(g)
$(CH_3)_2C(OH)CH_2O_2$	0.56	-1650	14.0	(a)
$(CH_3)_2C(OH)C(O_2)(CH_3)_2$			15.0	(c)
HO-*c*-$C_6H_{10}O_2$			22.4	(c),(h)
α-pinene-derived			20.9	(c),(i)
γ-terpinene-derived			19.7	(c),(i)
d-limonene-derived			21.2	(c),(i)
Hydroxyalkenyl				
isoprene-derived			17.4	(c),(j)
Alkoxyalkyl				
$CH_3OCH_2O_2$			~10	(k)
Oxoalkyl				
$CH_3C(O)CH_2O_2$			9.0	(a),(l)
Acyl				
$CH_3C(O)O_2$	~~31.4~~17.9	-~~580~~720	~~22~~20.0	(m)
$C_6H_5C(O)O_2$	110	-364	37.0	(a),(n)

Comments

[a] IUPAC Task Group recommendation (http://iupac.pole-ether.fr/); [b] Based on Rowley et al. (1992a; 1992b) and Boyd et al. (2003a); [c] Taken from Boyd et al. (2003a); [d] Mixture of $C_{10}H_{21}O_2$ radicals derived from the reaction of OH with decane; [e] Mixture of $C_{14}H_{29}O_2$ radicals derived from the reaction of OH with tetradecane; [f] Approximate value from Boyd et al. (1996), based on extrapolation of higher temperature data (393-426 K) using assumed value of E/R = -700 K; [g] Taken from Jenkin and Hayman (1995); [h] Derived from the reaction of OH with cyclohexene. RO_2 population dominated by β-hydroxy peroxy radical, HO-*c*-C_6H_{10}-O_2, formed from OH addition; [i] RO_2 population dominated by hydroxy peroxy radicals formed from OH addition to the given monoterpene; [j] Mixture of $HOC_5H_8O_2$ radicals derived from the reaction of OH with isoprene; [k] Approximate value from Jenkin et al. (1993a), based on steady state concentration of HO_2 formed from the self-reaction of $CH_3OCH_2O_2$ during modulated photolysis; [l] Based on Bridier et al. (1993); [m] $k_{298\,K}$ based on Groß et al. (2014)~~, and~~ Winiberg et al. (2016) and Hui et al. (2019). E/R ~~determined by correcting previously recommended value (-980 K [a]) for inferred effects of radical formation channel over the range 250-300 K~~based on Hui et al. (2019) (see Sect. S4); [n] Based on Roth et al. (2010).

Table 8. Branching ratios assigned to reaction channels (R6a)-(R6e) for reactions of hydrocarbon and oxygenated peroxy radical classes with HO_2 at 298 K.

Peroxy radical class	Channel branching ratio					Comment
	k_{6a}/k_6	k_{6b}/k_6	k_{6c}/k_6	k_{6d}/k_6	k_{6e}/k_6	
Alkyl (and default)	1.00	-	-	-	-	(a)
Acyl (R ≠ ~~phenyl~~aryl)	0.37	0.13	-	0.50	-	(b)
Acyl (R = ~~phenyl~~aryl)	0.65	0.15	-	0.20	-	(c)
β-Oxoalkyl (prim.)	0.82	-	-	0.18	-	(d)
β-Oxoalkyl (sec., tert.)	0.52	-	-	0.48	-	(e)
α-Alkoxyalkyl (prim., sec.)	0.54	-	0.26	-	0.20	(f)
α-Alkoxyalkyl (tert.)	1.00	-	-	-	-	(g)
β-Hydroxyallylic	0.92	-	-	0.08	-	(h)
β-Nitrooxyallylic	0.50	-	-	0.50	-	(i)

Comments

[a] Based on studies of CH_3O_2 and $C_2H_5O_2$ (as summarised by Orlando and Tyndall, 2012), and also used as a default in all cases other than those covered by comments (b)-(i); [b] 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 $C_2H_5C(O)O_2$; [c] Based on studies of $C_6H_5C(O)O_2$. k_{6d}/k_6 based on Dillon and Crowley (2008) and Roth et al. (2010), with other branching ratios based on those reported by Roth et al. (2010); [d] Based on studies of $CH_3C(O)CH_2O_2$ (Jenkin et al., 2008; Dillon and Crowley, 2008; Hasson et al., 2012); [e] Based on studies of $CH_3C(O)CH(O_2)CH_3$ (Dillon and Crowley, 2008; Hasson et al., 2012) and of $CH_3C(O)CH(O_2)CH_2OH$ (Praske et al. (2015). Praske et al. (2015) also reported possible minor contribution of channel (R6e) and/or (R6c) for $CH_3C(O)CH(O_2)CH_2OH$; [f] Based on studies of $HOCH_2O_2$ (Jenkin et al., 2007) and $CH_3OCH_2O_2$ (Jenkin et al., 2010). Contribution of OH formation in those studies was originally attributed to channel (R6d), but is allocated here to channel (R6e) on the basis of the theoretical study of Nguyen et al. (2010); [g] Full reaction is assigned to channel (R6a), because channels (R6c) and (R6e) are unavailable for tertiary radicals owing to the absence of an α- H atom; [h] Based on study of hydroxyallylic peroxy radicals formed in isoprene system by Liu et al. (2013), with support from the studies of Paulot et al. (2009) and Navarro et al. (2013); [i] Based on study of nitrooxyallylic radicals formed in isoprene system by Schwantes et al. (2015).

Table 9. Kinetic data for the self-reactions of hydrocarbon peroxy radicals. Where available, the temperature dependence is given by $k = A.\exp(-E/RT)$.

Peroxy radical	A	E/R	$k_{298\ \mathrm{K}}$	Comment
	(10^{-13} cm^3 molecule^{-1} s^{-1})	(K)	(10^{-14} cm^3 molecule^{-1} s^{-1})	
CH_3O_2	1.03	-365	35	(a)
Alkyl				
Primary				
$C_2H_5O_2$	0.76	0	7.6	(a)
n-$C_3H_7O_2$			30	(a)
n-$C_4H_9O_2$			40	(b)*
i-$C_4H_9O_2$			100	(b)*
n-$C_5H_{11}O_2$			39	(c)
neo-$C_5H_{11}O_2$	0.017	-1960	120	(d)
Secondary				
i-$C_3H_7O_2$	16	2200	0.1	(a)
sec-$C_4H_9O_2$			7	(b)*
sec-$C_5H_{11}O_2$			3.3	(c),(e)
sec-$C_{10}H_{21}O_2$			9.4	(c),(f)
sec-$C_{12}H_{25}O_2$			~14	(c),(f)
c-$C_5H_9O_2$	2.9	555	4.5	(g)*
c-$C_6H_{11}O_2$	0.77	184	4.2	(g)
Tertiary				
t-$C_4H_9O_2$	100	3900	0.0021	(a)
Allylic (alk-2-enyl)				
$CH_2{=}CHCH_2O_2$ (primary)	0.54	-760	69	(h)
~~Benzyl~~β-aryl				
$C_6H_5CH_2O_2$ (primary)	0.24	-1620	550	(a)

Comments

*Reported rate coefficient not corrected for the effects of secondary chemistry, which can lead to either an overestimate or underestimate of the rate coefficient; [a] IUPAC Task Group recommendation (http://iupac.pole-ether.fr/); [b] Taken from Glover et al. (2005); [c] Taken from Boyd et al. (1999); [d] Based on Lightfoot et al. (1990); [e] Mixture of 2-pentyl and 3-pentyl peroxy radicals ; [f] Mixture of secondary peroxy radicals of given formula; [g] Based Rowley et al. (1991;1992c); [h] Based on Jenkin et al. (1993b) and Boyd et al. (1996).

Table 10. Kinetic data for the self-reactions of oxygenated peroxy radicals. Where available, the temperature dependence is given by $k = A.\exp(-E/RT)$.

Peroxy radical	A	E/R	$k_{298\,K}$	Comment
	(10^{-13} cm^3 molecule^{-1} s^{-1})	(K)	(10^{-14} cm^3 molecule^{-1} s^{-1})	
α-Hydroxyalkyl				
$HOCH_2O_2$ (primary)			620	(a)
β-Hydroxyalkyl				
Primary				
$HOCH_2CH_2O_2$	0.78	-1000	220	(a)
$(CH_3)_2C(OH)CH_2O_2$	0.14	-1740	480	(a)
Secondary				
$CH_3CH(OH)CH(O_2)CH_3$	0.077	-1330	67	(a)
HO-*c*-$C_6H_{10}O_2$			120	(b)
Tertiary				
$(CH_3)_2C(O_2)CH_2OH$			1.5	(b)
$(CH_3)_2C(OH)C(O_2)(CH_3)_2$	5.9	1420	0.5	(c)
HO-*c*-$C_6H_8(CH_3)_2O_2$			2.0	(b)
Hydroxyallylic (hydroxyalk-2-enyl)				
Primary				
$HOCH_2CH{=}CHCH_2O_2$ (δ-hydroxy)			280	(d)
$HOCH_2C(CH_3){=}C(CH_3)CH_2O_2$ (δ-hydroxy)			390	(d)
Secondary				
$HOCH_2CH(O_2)CH{=}CH_2$ (β-hydroxy)			570	(d)
Tertiary				
$HOCH_2C(CH_3)(O_2)C(CH_3){=}CH_2$ (β-hydroxy)			6.9	(d)
Alkoxyalkyl				
$CH_3OCH_2O_2$ (primary)			210	(a)
β-Oxoalkyl				
$CH_3C(O)CH_2O_2$ (primary)			800	(a)
γ-Oxoalkyl				
$CH_3C(O)C(CH_3)_2CH_2O_2$ (primary)			480	(e)
t-$C_4H_9C(O)C(CH_3)_2CH_2O_2$ (primary)			460	(e)
Acyl				
$CH_3C(O)O_2$	29	-500	1600	(a)
$C_2H_5C(O)O_2$			1700	(a)
$(CH_3)_2CHC(O)O_2$			1440	(f)
$(CH_3)_3CC(O)O_2$			1440	(f)
$C_6H_5C(O)O_2$	3.4	-1110	1400	(a)
Alkoxyacyl				
$CH_3OC(O)O_2$ (and $HC(O)OCH_2O_2$)			2300	(g)

Comments

[a] IUPAC Task Group recommendation (http://iupac.pole-ether.fr/); [b] Taken from on Boyd et al. (2003b); [c] Based on Jenkin and Hayman (1995) and Boyd et al. (1997); [d] Taken from Jenkin et al. (1998); [e] Based on Le Crâne et al. (2006); [f] Based on Tomas and Lesclaux (2000) and Le Crâne et al. (2004); [g] Taken from Hansen et al. (2003). The kinetics of the two peroxy radicals formed from the reaction of Cl or F with methyl formate reported to possess indistinguishable kinetics.

Table 11. Kinetic data for the cross-reactions of hydrocarbon or oxygenated peroxy radicals at 298 K. Where available, the temperature dependence expression is given in the comments.

Peroxy radical 1	Peroxy radical 2	$k_{298\ \mathrm{K}}$ (10^{-13} cm^3 molecule^{-1} s^{-1})	Comment
CH_3O_2	$C_2H_5O_2$	2	(a)
	neo-$C_5H_{11}O_2$	15	(b)
	c-$C_6H_{11}O_2$	~~0.9~~1.0	(~~b~~c)
	t-$C_4H_9O_2$	0.031	(a),(~~c~~d)
	$CH_2{=}CHCH_2O_2$	17	(b),(~~d~~e)
	$C_6H_5CH_2O_2$	< 20	(b)
	$CH_3C(O)CH_2O_2$	38	(a)
	$CH_3C(O)O_2$	110	(a),(~~e~~f)
$C_2H_5O_2$	*neo*-$C_5H_{11}O_2$	5.6	(b)
	c-$C_6H_{11}O_2$	0.4	(b)
	$CH_3C(O)O_2$	100	(b)
	$C_2H_5C(O)O_2$	120	(a)
$CH_3C(O)O_2$	$CH_3C(O)CH_2O_2$	50	(a)
	c-$C_6H_{11}O_2$	104	(~~f~~g)
	t-$C_4H_9O_2$	111	(~~f~~g)
	sec-$C_{10}H_{21}O_2$	109	(~~f~~g)
	sec-$C_{12}H_{25}O_2$	105	(~~f~~g)
HO-*c*-$C_6H_9(CH_3)O_2$ (secondary)	HO-*c*-$C_6H_9(CH_3)O_2$ (tertiary)	6.2	(~~g~~h)
$HOCH_2CH{=}CHCH_2O_2$	$HOCH_2CH(O_2)CH{=}CH_2$	39	(~~h~~i)
$HOCH_2C(CH_3){=}C(CH_3)CH_2O_2$	$HOCH_2C(CH_3)(O_2)C(CH_3){=}CH_2$	25	(~~h~~i)

Comments

[a] IUPAC Task Group recommendation (http://iupac.pole-ether.fr/); [b] Taken from Villenave et al. (1996); [c] Based on Villenave et al. (1996) and Nozière and Hanson (2017); [~~c~~d] Temperature dependence expression is 3.8 × 10^{-13} exp(-1430/*T*); [~~d~~e] Temperature dependence expression is 2.8 × 10^{-13} exp(515/*T*) ; [~~e~~f] Temperature dependence expression is 2.0 × 10^{-12} exp(500/*T*); [~~f~~g] Taken from Villenave et al. (1998); [~~g~~h] Taken from Boyd et al. (2003b). The structures refer to the isomeric secondary and tertiary peroxy radicals formed from the addition of OH to 1-methylcyclohexene; [~~h~~i] Taken from Jenkin et al. (1998). Presented values are limited to those reported for the cross reactions of the major radicals formed from the terminal addition of OH to buta-1,3-diene and the terminal addition of OH to 2,3-dimethyl-buta-1,3-diene.

Table 12. Substituent activation factors applied to self-reaction rate coefficients, based on Eq. (16).

Substituent	α	β	Comment
alkyl	1.00	0	(a)
β-hydroxy	8.0×10^{-5}	0.4	(b)
allylic (alk-2-enyl)	4.0×10^{-2}	0.15	(c)
~~Benzyl~~β-aryl	5.8×10^{-2}	0.15	(d),(e)
α-alkoxy	7.0×10^{-5}	0.4	(f),(g)
β-oxo	1.6×10^{-4}	0.4	(h),(g)
γ-oxo	5.3×10^{-5}	0.4	(i),(g)

Comments

[a] α = 1.00 and β = 0 by definition for alkyl peroxy radicals. These are also used as a default for peroxy radical classes not covered by comments (b)-(i), with the exception of acyl peroxy radicals (discussed in Sect. 2.6); [b] Based on data for β-hydroxyalkyl peroxy radicals in Table 10; [c] Based on data for allylic and δ-hydroxyallylic peroxy radicals in Tables 9 and 10; [d] Based on data for $C_6H_5CH_2O_2$ (Table 9); [e] β assumed equivalent to that for allylic substituent; [f] Based on data for $CH_3OCH_2O_2$ (Table 10); [g] β assumed equivalent to that for β-hydroxy substituent; [h] Based on data for $CH_3C(O)CH_2O_2$ (Table 10); [i] Based on data for γ-oxoalkyl peroxy radicals in Table 10.

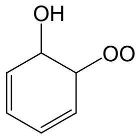
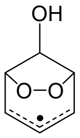
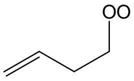
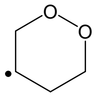
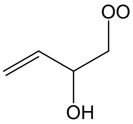
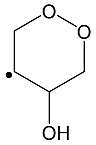
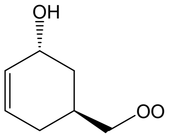
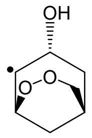
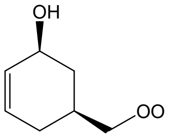
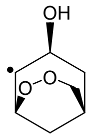
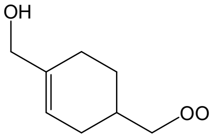
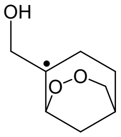
Table 13. Branching ratios assigned to parameterized permutation reactions of RO_2 (see text).

Peroxy radical class	Channel branching ratio			Comment
	k_{9a}/k_9	k_{9b}/k_9	k_{9c}/k_9	
CH_3O_2	$7.2 \times \exp(-885/T)$	$(1-(k_{9a}/k_9))/2$	$(1-(k_{9a}/k_9))/2$	(a)
Primary and secondary	0.6	0.2	0.2	(b)
Tertiary and acyl	0.8	-	0.2	(c)

Comments

[a] Based on IUPAC Task Group recommendation for the CH_3O_2 self-reaction (http://iupac.pole-ether.fr/). An alternative representation using temperature-dependent channel rate coefficients is provided in Sect. S5; [b] Based on a rounded mean of the reported 298 K branching ratios for the self-reactions of $C_2H_5O_2$, i-$C_3H_7O_2$, $HOCH_2CH_2O_2$, $(CH_3)_2C(OH)CH_2O_2$, $CH_3C(O)CH_2O_2$, $CH_3OCH_2O_2$, and $C_6H_5CH_2O_2$ based on IUPAC Task Group recommendations (http://iupac.pole-ether.fr/); *neo*-$C_5H_{11}O_2$, c-$C_6H_{11}O_2$ and $CH_2{=}CHCH_2O_2$, based on Lightfoot et al. (1990), Rowley et al. (1991), Jenkin et al. (1993a ; 1993b) and Boyd et al. (1996); and for the self- and cross- reactions of primary and secondary RO_2 formed from reactions of OH with conjugated dienes (Jenkin et al., 1998); [c] Based on a rounded mean of the reported 298 K branching ratios for the following cross-reactions: $CH_3C(O)O_2$ + CH_3O_2, $C_2H_5C(O)O_2$ + $C_2H_5O_2$ and $CH_3C(O)O_2$ + $CH_3C(O)CH_2O_2$, based on IUPAC Task Group recommendations (http://iupac.pole-ether.fr/); and $HOCH_2C(CH_3)(O_2)C(CH_3){=}CH_2$ + $HOCH_2C(CH_3){=}C(CH_3)CH_2O_2$ formed from reaction of OH with 2,3-dimethyl-buta-1,3-diene (Jenkin et al., 1998).

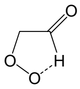
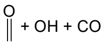
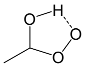
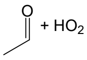
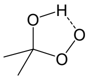
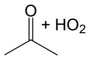
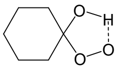
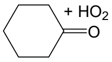
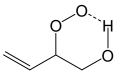
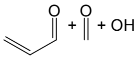
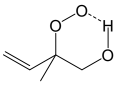
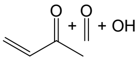
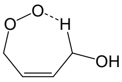
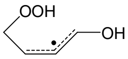
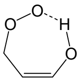
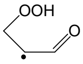
Table 14. Representative ~~R~~rate coefficients ~~assigned to~~for template ring-closure reactions of peroxy radicals [a].

Radical	Product		*A*	*E*/*R*	$k_{298\,\mathrm{K}}$	Comment
			($\mathrm{s^{-1}}$)	(K)	($\mathrm{s^{-1}}$)	
			-	-	**(3.6-2500) × 10^2**	(b)
		***sec.*** [c]	**1.0 × 10^{10}**	**8140**	**0.014**	(d)
		tert.	1.0 × 10^{10}	7740	0.053	(e)
		*sec.*	1.0 × 10^{10}	7740	0.053	(e)
		tert.	**1.0 × 10^{10}**	**7340**	**0.20**	(f)
		*sec.*	4.8 × 10^{10}	7850	0.17	(e)
		tert.	**4.8 × 10^{10}**	**7450**	**0.67**	(g)
		*sec.*	4.8 × 10^9	6750	0.70	(e)
		tert.	**4.8 × 10^9**	**6350**	**2.7**	(h)
		***tert.***	**1.4 × 10^{10}**	**7100**	**0.63**	(i)

Comments

[a] Temperature dependence of rate coefficient given by $k = A \exp(-(E/R)/T)$. Rapid reaction of the product radical with O_2 dominates over the reverse ring-opening reaction under atmospheric conditions. Entries in bold font are based on reported data for the specific or closely-related structures, with other entries inferred using assumptions given in the following comments; [b] Range of 298 K values based on the calculations of Raoult et al. (2004), Glowacki et al. (2009) and Olivella et al. (2009) for the dominant conformer of the example peroxy radical, formed during the oxidation of benzene. Based on these data, and data for other aromatic systems, analogous ring-closure reactions are assumed to be the exclusive fates of corresponding peroxy radicals formed during the oxidation of aromatic hydrocarbons (Jenkin et al., 2018b); [c] Denotes substitution of product radical; [d] Based on information reported by Vereecken and Peeters (2004) for calculations for the given peroxy radical; [e] *E*/*R* for formation of a tertiary radical assumed to be 400 K lower than for formation of a secondary radical, corresponding to a difference in *E* of ≈ 3.3 kJ $\mathrm{mol^{-1}}$. This is consistent with differences in energy barriers reported for formation of secondary and tertiary radicals (Vereecken and Peeters, 2004); [f] Based on the calculations of Vereecken and Peeters (2004) for a relevant tertiary peroxy radical formed during the oxidation of isoprene; [g] Based on the calculations of Vereecken and Peeters (2004) for a relevant tertiary peroxy radical formed during the oxidation of α-pinene. Applies specifically to *anti-* conformers, when the OH and peroxy radical groups on the opposite sides of the ring (as shown), which were calculated to account for 60 % of the *anti-* + *syn-* population (Vereecken and Peeters, 2004); [h] Based on the calculations of Vereecken and Peeters (2004) for a relevant tertiary peroxy radical formed during the oxidation of α-pinene. Applies specifically to *syn-* conformers, when the OH and peroxy radical groups on the same side of the ring (as shown), which were calculated to account for 40 % of the *anti-* + *syn-* population (Vereecken and Peeters, 2004); [i] Based on the calculations of Vereecken and Peeters (2004) for the a relevant tertiary peroxy radical, formed during the oxidation of β-pinene; [h]

Table 15. Representative r~~R~~ate coefficients ~~assigned to~~for selected H-shift isomerization reactions of peroxy radicals.

Radical	Product(s)	$k(T)$	$k_{298\,K}$	Comment
		(s^{-1})	(s^{-1})	
1,4 formyl H-shift				
		$3.0 \times 10^{7} \exp(-5300/T)$	~~5.7~~0.57	(a),(b)
1,4 hydroxyl H-shift				
		$3.6 \times 10^{12} \exp(-6310/T)$	2.3×10^{3}	(b),(c)
		$6.7 \times 10^{12} \exp(-5780/T)$	2.5×10^{4}	(b),(d)
		$5.6 \times 10^{12} \exp(-6010/T)$	9.8×10^{3}	(b),(e)
1,5 hydroxyl H-shift				
		$1.9 \times 10^{11} \exp(-9750/T)$	1.2×10^{-3}	(b),(f)
		$1.0 \times 10^{11} \exp(-9750/T)$	6.2×10^{-4}	(b),(f)
1,6 hydroxyalkyl H-shift				
		$1.3 \times 10^{10} \exp(-8380/T) \times \exp(10^{8}/T^{3})$	3.5×10^{-1}	(g)
1,6 enol H-shift				
		$2.4 \times 10^{-1}\, T^{4.1} \exp(-2700/T)$	3.9×10^{5}	(h)

Comments

[a] Based on rate coefficient reported for the methacrolein-derived peroxy radical, $HOCH_2C(CH_3)(O_2)C(=O)H$, by Crounse et al. (2012). Applied to primary, secondary and tertiary α-formyl peroxy radicals; [b] The initially-formed hydroperoxy-substituted product radical decomposes spontaneously to produce the displayed products; [c] Based on the rate coefficient estimated for $CH_3CH(OH)O_2$ by Hermans et al. (2005); Applied to secondary α-hydroxyl peroxy radicals; [d] Based on the rate coefficient estimated for $(CH_3)_2C(OH)O_2$ by Hermans et al. (2005); Applied to tertiary α-hydroxy peroxy radicals; [e] Based on the rate coefficient estimated for *cyclo*-$C_6H_{10}(OH)O_2$ by Hermans et al. (2005); Applied generally to cyclic α-hydroxy peroxy radicals (i.e. where the OH and OO groups are substituents to a ring); [f] Based on rate coefficients reported by Peeters et al. (2014) for corresponding unsaturated secondary and tertiary β-hydroxy peroxy radicals formed in isoprene oxidation. Applied generally to unsaturated β-hydroxy peroxy radicals containing the sub-structures shown; [g] Based on the geometric mean of rate coefficients applied to (*Z*)-$CH(OH)C(CH_3)=CHCH_2O_2$ (CISOPAO2) and (*Z*)-$CH(OH)CH=C(CH_3)CH_2O_2$ (CISOPCO2) in MCM v3.3.1 (Jenkin et al., 2015), based on the calculations of Peeters et al. (2014) and observations of Crounse et al. (2011). 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). Rapid reaction of the product radical with O_2 dominates over the reverse isomerization reaction under atmospheric conditions; [h] Based on the geometric mean of rate coefficients reported for (*Z*)-$HOCH=C(CH_3)CH(O_2)CH_2OH$ and (*Z*)-$HOCH=CHC(CH_3)(O_2)CH_2OH$ in the calculations of Peeters and Nguyen (2012). Applied to peroxy radicals containing the sub-structure shown. Rapid reaction of the product radical with O_2 dominates over the reverse isomerization reaction under atmospheric conditions.