Authors' responses to referee and discussion comments on: Jenkin et al., Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2018-146, 2018.

We are very grateful to the referees and commenter 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).

A. Comments by Referee 1

Opening comments:

I applaud the authors for tackling this messy and complex problem. This is a valuable paper and should be published; ACP is an appropriate journal for this manuscript. The authors have laid out the case well, described the methodology in great detail, and been transparent about assumptions. While the lack of data for some configurations makes it difficult to develop robust generalizations for similar structures, especially in product distribution, it is valuable to have a protocol. The authors present one that is vastly improved over what we have now (basically nothing generalizable). I hope that the community assists in improving this by collecting more data to help extend and evaluate the subsequent reaction pathways of the less-studied oxygenated aromatics and their products.

A valuable component of this paper is the development of site-specific attack distribution and prediction of resulting product structures. This is necessary for so many issues – yield of ozone per molecule of VOC, yield of SOA (and developing a mechanistic aerosol mechanism), source attribution based on secondary products, etc. The focus is on automated detailed mechanisms but it would also be useful for people trying to write balanced chemical equations for individual chemicals. It's surprising how good the yields are in Figure 5.

Response: We are very grateful to the referee for these very positive and supportive comments on our work.

Comment A1: The illustration of calculating SARs for several molecules is valuable; it should be referenced in the main paper somewhere - I cannot find a mention of it. The method for aromatics is different enough than previously applied for simpler molecules, including the additional correction factors (i.e. the exp(140/T) for additional methyl groups; substituent adjustment factors; the use of alternate k values), thus directing readers to the end of SI would help make it clearer (versus them finding their own way to the end of it). In the examples, it would be useful to explicitly list where R=1 or F=1, for example: in the (b) carbon of p-cymene, I'm assuming it should be ktert*F(CH3)*F(CH3)*F(Ph2), where F(CH3)=1 so it is not shown? Also would be informative to see an example of the calculations for addition reactions of O2 to OH-aromatic adducts (I didn't calculate the same distribution of cresols as reported – likely misinterpreting how substituent factors are applied in this case).

Response: We agree that clearer reference to the example SAR calculations would be helpful. Reference was originally made in Sect. 3.1.1 to the calculations for methyl-substituted aromatic hydrocarbons in the Supplement. Similarly to that in the preceding companion paper, the following statement has now also been added to the description of the scope of the paper in the Introduction (new text in red font):

> "….. In each case, the rate coefficient is defined in terms of a summation of partial rate coefficients for H atom abstraction or OH addition at each relevant site in the given organic compound, so that the attack distribution is also defined. This is therefore the first generalizable SAR for reactions of OH with aromatic compounds that aims to capture observed trends in rate coefficients and the site-specificity of attack. Application of the methods is illustrated with examples in the Supplement."

Although the example SAR calculations are located towards the end of the Supplement, they are also clearly advertised in the contents list on page 1 of the Supplement.

The referee makes a valid point about the omission of the unity F(-CH_3) factor in the example OH + aromatic calculations, and this has been included in the revised Supplement to improve clarity. We also agree with the referee concerning the inclusion of example calculations for the subsequent reaction sequences initiated by reaction with O_2. Full illustration of the complete reaction sequences following the reaction of OH with toluene has now been included in the Supplement, with reference to this at the end of Sect. 4.1, as follows:

> "Sect. S6 provides example calculations for the methods described above for the chemistry initiated by reaction of O_2 with the OH-aromatic adducts formed from the addition of OH to toluene."

Comment A2: For phenols and cresols, the authors recommend using experimental data when available. Are there other configurations where experimental data should override the estimates?

Response: Estimation methods are generally used to fill in (the often large) gaps in knowledge, where experimental data is unavailable. As a general rule, therefore, a recommended parameter based on evaluated experimental data for a specific reaction should always override an estimated parameter – even if methods based on SARs are initially used to construct a highly detailed mechanism for efficiency. A statement to this effect is actually included in Sect. 3.2.1, where phenol and the cresols are discussed. In the present work, the estimated parameters were generally found to be very close to the recommendations. Although the estimated rate coefficients and attack distributions for phenol and the cresols recreate some of the features inferred from reported experimental studies, we judged that the deviations were sufficient that it was helpful to emphasise this point and also to provide recommended attack distributions based on experimental information.

Below, are some specific comments:

Comment A3: Page 4, line 1: would be helpful to kprim, ksec and ktert so that reader does not have to search through another paper – could add to Table 1, or list in text. Perhaps add kabs(OH). The 2018a paper is a critical companion paper, but this one should also stand mainly on its own.

Response: The paragraph the referee is referring to provides an overview of the relevant information for saturated organic compounds that can be found in the preceding companion paper. In addition to k_{prim}, k_{sec} and k_{tert}, this includes a (potentially large) number of neighbouring group parameters, F(X), and a series of generic rate coefficients for reactions at oxygenated groups, including $k_{abs(-OH)}$ (as summarised in the relevant paragraph). We judged that reproduction of all this information could not be justified, and that it would be artificial and misleading to reproduce a subset of it in the present paper (e.g. only those parameters mentioned in the first line of the paragraph, as suggested by the referee). In some respects, the companion paper serves as fully-referenced supporting information, and we feel this is sufficient and appropriate.

Comment A4: Table 1: It took me a while to figure out that "substituent" is not the neighboring group (i.e. not the "X" in Kwok and Atkinson tables), but the successive carbons in the alkyl group, and the "X" is the aromatic ring. Adding F(-CH3) and other groups might help – or state that readers can find these other Fs in the 2018a paper.

Response: The use of the term "substituent" for both the substituent group on the aromatic ring and generally for the neighbouring group in the Kwok and Atkinson method is unfortunate. It is difficult to see a way to change this, because both are common and valid uses of the term.

For clarification here, the parameters F(-Ph1) and F(-Ph2) in the present work are completely analogous to the parameter (or substituent factor) F(-C_6H_5) in Table 2 of Kwok and Atkinson (1995), and apply when H atom abstraction is occurring from the carbon atom adjacent to the aromatic ring (i.e. in a substituent to the aromatic ring). In the present work, we found it was necessary to define the two parameters, F(-Ph1) and F(-Ph2), with each applying to a different set of substituents to the aromatic ring. Thus, column 1 identifies the relevant substituent to the aromatic ring from which abstraction is occurring; and column 2 gives the relevant parameter (or neighbouring group substituent factor) that is applied in each case to account for the neighbouring aromatic group effect. Although at first sight this is possibly a little confusing, we feel that the context in the associated text and the information given in the comments to the table should clarify the approach.

In view of the referee's comment, we have slightly changed the table caption to remove the double use of the term "substituent". This now reads:

> "Neighbouring group factors, F(X), for α- H-atom abstraction from substituents in aromatics, and their temperature dependences described by $F(X) = A_{F(X)} \exp(-B_{F(X)}/T)$."

Comment A5: Table 3: If the OH addition is on an ipso carbon of a compound with 3 substituents, I assume one uses the substituent factor for just the other 2 substituents (i.e. number of substituents = 2). Might state that in the paper. Title of Table 3 reads "Each factor relates to the combination of methyl substitutions", but it also relates to other functional groups.

Response: We are pleased that the referee has understood the method correctly. We believe the point being made is already clearly stated in Sect. 3.1.1, just after Eq. (4), where the following text appears:

> "……where k is either k_{arom} or k_{ipso} and F(Φ) is a factor that accounts for the effect of the combination of methyl substituents in the molecule in terms of their positions (i.e. *ortho*-, *meta*- or *para*-) relative to each OH addition location."

The omission of an effect of the *ipso*- substituent within F(Φ) is logical, because the product radical is delocalized over the carbon atoms *ortho*-, *meta*- and *para*- to the OH addition location (e.g. see Fig. 3).

The same statement about F(Φ) is also made in the caption to Table 3, where the F(Φ) values are presented. These values are specific to the combination of methyl substituents. The referee is correct that these values are also used (modified by the adjustment factors, R(Φ), in Table 6) for other substituents. We feel this is already very clearly explained, and that it would be confusing to state that the parameters in Table 3 also apply to other substituents.

Comment A6: Page 4, line 20: I don't know if H-abstraction is "minor", if you later present it (Table 4) as 3-22%.

Response: The text being referred to on page 4 concerns *methyl-substituted aromatics* (Sect. 3.1.1) for which the contributions of H abstraction are reported to vary from 4 % for *m*-xylene to 13.7 % for hexamethylbenzene (Table 4), these generally being reported as "minor contributions" in the cited studies. We feel that the calculated H atom abstraction contribution for *p*-cymene of 22 %, quoted by the referee, probably also classifies as minor. However, this is discussed in the subsequent section on *higher alkyl-substituted aromatics* (Sect. 3.1.2) and is not encompassed by the statement on page 4 and therefore not relevant. Clearly if a substituent is large enough, H abstraction from that substituent can make a major contribution.

Comment A7: Page 5, equation 4: shouldn't this be kadd*F(phi)*R(phi)? R is not needed until later, and not introduced until Table 6, but Table 6 does include R for methyl=1, so this would better generalize the equation.

Response: The referee raises a valid point. However, we feel it is clearer to delay introducing and discussing the adjustment factors, R(Φ), until they are required in later sections. The unity value presented for CH_3 in Table 6 is included for completeness, and emphasizes that it is a reference case. In view of the referee's comment (and comment B7 of referee 2) we have now formalised the method as suggested, with inclusion of R(Φ) in Sect. 3.1.2 on *higher alkyl-substituted aromatics*, as follows:

> "Table 6 shows a set of adjustment factors for non-methyl substituents, R(Φ), that represent corrections to the values of F(Φ) in Table 3 (and to k_{ipso}, when appropriate), such that:
>
> $$k_{add} = \Sigma k \, F(\Phi) \, R(\Phi) \quad (5)$$"

Comment A8: Page 8, line 5: So you totally ignore the aromatic carbons and use the estimated rate for the alkenyl group?

Response: We are very grateful to the referee for alerting us to this omission. As stated earlier in the section, addition to the aromatic ring is assumed to be completely deactivated in styrenes, based on a number of reported studies. However, for alkenyl-substituted aromatics containing more remote

C=C bonds, this would not be expected, although there are apparently no data to test this. The relevant text has therefore been adjusted as follows:

> "The addition of OH to more remote C=C bonds in substituent groups in alkenyl-substituted aromatic hydrocarbons is expected to be well described by the methods described in the companion paper (Jenkin et al., 2018a), which update and extend the methods reported by Peeters et al. (2007) for alkenes and dienes. However, there are currently no data to test this assumption. In these cases, it is suggested that a default value of R(Φ) = 1.0 for the remote alkenyl group is applied for addition of OH to the aromatic ring."

Technical corrections/comments:

Page 5, line 18: Can't see that you defined kcalc , assume it is the same as k, defined as k=kadd+kabs (page 3, line 17)

Response: The referee is correct. The definition on page 3 has been amended to "$k_{calc} = k_{add} + k_{abs}$."

Consider replacing the "." in equations with "·" or "x" to signify multiplication. It looks like a period.

Page 8, line 2: replace reference to Table 3 with Table 6.

Page 9, line 8: replace "upper panel" with "large panel" or "main panel".

Response: We are very grateful to the referee for identifying the above typos and technical corrections, which have all been corrected in the revised manuscript.

B. Comments by Referee 2

General comments:

This manuscript describes the development of a structure-activity relationship (SAR) model for the reactions of OH with aromatic organic compounds which is explicit in terms of the OH reaction mechanism, and in subsequent reactions with molecular oxygen. These features likely will assist in the development of more detailed and quantitively correct representations of the atmospheric oxidation mechanisms for aromatic compounds. The work is carefully planned and performed, and the topical nature of the work makes it quite appropriate for publication in the Atmospheric Chemistry and Physics. The supporting information is very through and includes all experimental and calculated rate constant values, as well as examples to help the reader calculate rate constants from the SAR parameters.

Response: We are very grateful to the referee for these very positive and supportive comments on our work.

Specific comments

Comment B1: p.2: It would be good to note as a motivation that there really isn't a generalizable OH + aromatic SAR currently available in the literature.

Response: We thank the referee for this suggestion. This point has now been made in the description of the scope of the paper in the introduction:

> "….. In each case, the rate coefficient is defined in terms of a summation of partial rate coefficients for H atom abstraction or OH addition at each relevant site in the given organic compound, so that the attack distribution is also defined. This is therefore the first generalizable SAR for reactions of OH with aromatic compounds that aims to capture observed trends in rate coefficients and the site-specificity of attack. Application of the methods is illustrated with examples in the Supplement."

Comment B2: p. 5, line 11: I assume from this discussion that the regression didn't use the experimental uncertainties in the rate constants to weight the individual values. Was anything done to take into account that the experimental rate constants have varying uncertainties?

Response: The referee is correct that different uncertainties were not assigned to the contributory preferred rate coefficients used in the analysis. We are also not aware of this being done in previous SAR development studies (e.g. Kwok and Atkinson, 1995; Calvert et al., 2008; 2011; Peeters et al., 2007). In practice it is very difficult to assign objective compound-specific uncertainties, because most preferred values are derived from a number of contributing studies (some absolute and some relative rate) for which the quoted rate coefficients do not themselves have uncertainties reported consistently, such that a subjective judgement is required. The relative rate determinations are of course also influenced by uncertainties in the value of the reference rate coefficient. Using the IUPAC preferred values for benzene and toluene at 298 K as examples, these are each judged to have an uncertainty of a factor of about 1.25 by the IUPAC Task Group, although this is not based on a rigorous statistical analysis[1]. The former preferred value is based on the unweighted average of 9 determinations (all absolute) and the latter on the unweighted average of 11 determinations (5 absolute and 6 relative rate). Based on inspection of the preferred values for the other methyl-substituted aromatics (and the contributing studies), we judge that these determinations are unlikely to have uncertainties significantly greater than a factor of 1.25, such that a standard unweighted least squares analysis is justifiable.

Comment B3: p. 5, line 13: The comment about ortho- and para-substituents being more activating than meta-substituents is only true for the specific case of electron donating substituents such as methyl groups, which is also a well-known property of electrophilic aromatic substitution reactions.

Response: We thank the referee for this clarification.

Comment B4: Various tables: Why aren't uncertainties given for the various F(phi) values determined from the fitting process?

Response: In common with all previous SAR development studies for atmospheric reactions that we are aware of (e.g. Kwok and Atkinson, 1995; Peeters et al., 2007; Calvert et al., 2008; 2011; Ziemann and Atkinson, 2012), we have chosen not to report uncertainties in the optimized parameters. This is because the calculation of a rate coefficient generally requires the use of several parameters, the values of which are not independent. Thus, it is not valid to vary the applied value of a given parameter within its uncertainty bounds, without making a compensating change in another parameter – and an assessment of the overall uncertainty in the final value of k_{calc} using combination and propagation of errors would not give a reliable estimate. Thus, although the optimized parameters are subject to uncertainties, these are generally not of practical value in applying the SAR. In practice, the performance of a SAR is mainly governed by the assumptions in the model framework that forms its basis, and the optimized parameters simply specify how to get the best performance out of the method within the constraints of the model framework. This performance is therefore generally assessed and improved by testing and refining the model and optimised parameters as the kinetics database expands and improves.

Comment B5: p. 6 line 16: I don't understand the problem being described here. From the statement earlier in this paragraph, I thought the H-abstraction values were being determined from p-cymene (the only compound for which H-abstraction experimental information is available), so I don't understand why these parameters then need to be adjusted.

Comment B6: Additionally, on what theoretical grounds might these adjustments be justified?

Response: We do not fully understand the point the referee is making. With reference to the parameters in Table 1, the relevant paragraph is explaining that the neighbouring group parameter F(-Ph1) optimized for H atom abstraction from -CH_3 substituents does not give a good description of the reported contribution of H atom abstraction from the *i*-propyl substituent in *p*-cymene (and likely other larger substituents); and that it is therefore necessary to define a further parameter, F(-Ph2), for H atom abstraction from -CH_2- and -CH< substituents, based on the *p*-cymene data. Although F(-Ph2) is being introduced as a new parameter on this basis, there is no subsequent adjustment being described.

Comment B7: p. 6 line 30: The equation for R(phi) should be explicitly given.

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[1] http://iupac.pole-ether.fr/htdocs/supp_info/Guide_to_Gas-Phase_Datasheets_Final_Oct_2017.pdf

Response: We thank the referee for this suggestion (see also comment A7 of referee 1). We have now formalised the method at this point, as suggested:

> "Table 6 shows a set of adjustment factors for non-methyl substituents, R(Φ), that represent corrections to the values of F(Φ) in Table 3 (and to k_{ipso}, when appropriate), such that:
> $k_{add} = \Sigma k\ F(\Phi)\ R(\Phi)$ (5)"

Comment B8: Table 5: I understand that previous reports used different definitions for the branching ratio, but it is quite distracting and confusing to have two sets of values reported. I suggest that the authors convert all branching ratios to a common definition and to report that single set of values.

Response: We thank the referee for this suggestion. In the revised manuscript, we present all branching ratios relative to k_{add} in Table 5. Where the original reference reports values relative to $k_{add} + k_{abs}$, we also give the reported values in a footnote.

Comment B9: The form of equation 5 should be justified in the text.

Response: We agree with the referee's comment, and provide more explanation of the form of this equation in the revised manuscript. Following submission of the manuscript, we also realised that the previously declared equation (now Eq. (7)) did not describe the applied method for the case of $n = 0$, and we apologise for this omission. The relevant material has therefore been changed to read as follows:

> "The value of $k_{abs\text{-}O2}$ is assumed to be independent of the presence of alkyl substituents, but the value of $k_{add\text{-}O2}$ depends on both the degree and distribution of alkyl substituents, and is given by:
>
> $k_{add\text{-}O2} = k°_{add\text{-}O2} \prod F_i(X)$, for $n = 0$ (or 1) (6)
>
> $k_{add\text{-}O2} = k°_{add\text{-}O2} \prod F_i(X)/n^{0.5}$, for $n \geq 1$ (7)
>
> Here, n is the number of alkyl substituents (in positions 1 to 5 relative to the addition of O_2), and $F_i(X)$ is the activating effect of each alkyl substituent in terms of its position (see Fig. 3). The assigned values of $F_i(X)$ (given in Table 8) recreate the reported general trend in total hydroxyarene yields for methyl-substituted aromatics, and also a reasonable representation of the reported distribution of isomers formed from a given aromatic precursor (see Table S1). In the case of the toluene system, for example, the optimized parameters provide respective yields of 12.2 %, 3.7 % and 3.3 % for *o*-, *m*- and *p*-cresol, and a total rate coefficient of 5.7×10^{-16} cm^3 molecule^{-1} s^{-1} for the reaction of O_2 with the set of OH-toluene adducts (i.e. HOC_7H_8) at 298 K; in very good agreement with the IUPAC recommendations (IUPAC, 2017c). To a first approximation, the simpler expression in Eq. (6) provides an acceptable description for the complete series of aromatics, but leads to a systematic underestimation of the hydroxyarene yields reported for *m*-xylene, *p*-xylene, 1,2,4-trimethylbenzene and 1,3,5-trimethylbenzene. The adjusted expression in Eq. (7) is therefore defined to allow a more precise description of the reported hydroxyarene yields for the more substituted species."

Eq. (6) shows that $k_{add\text{-}O2}$ is simply determined from the product of the reference value, $k°_{add\text{-}O2}$ (defined earlier), and the value of $F_i(X)$ for each alkyl substituent. The need for the extra term, $n^{0.5}$, in Eq.(7) is now explained and justified in the new text.

Comment B10: Table S3: The authors should use the term "calculated" rather than "estimated" to be consistent with the other instances where rate constants calculated from the SAR model are reported. I understand that the red font entries in the "recommended" column are experimental values, but for the non-red font entries, what is the process for the determination of these recommended values?

Response: We thank the referee for pointing out this inconsistency, which has been corrected in the revised manuscript. Regarding explanation of the recommended values, the final column in Table S3 refers the reader to footnotes at the end of the table which explain how both the red font and non-red font entries were assigned. The non-red font channel contributions mainly retain the calculated relative importance, but with their absolute contributions reduced to account for the (minor) residual not covered by the yields of the products reported in experimental studies.

Comment B11: Figure 7: To what extent is the lower uncertainty evident in the aromatic set of compounds as compared to the aliphatic compounds a function of larger structural/functional group heterogeneity of the aliphatic compound group? Or is there another explanation?

Response: As stated by the referee, the lower uncertainty for the aromatic species reflects that the larger database of aliphatic compounds contains a more diverse set of oxygenated species, such that additional data for aromatic oxygenated species would be valuable. We believe this is already covered by the text in Sect. 6, where Fig. 7 is referred to:

> "……This shows a similar pattern to that reported previously for the much larger dataset of aliphatic species (Jenkin et al., 2018a), but with systematically lower errors. As described in Sect. 3.2, some of the classes of aromatic oxygenated species contain data for only a single compound, such that the optimized parameters inevitably provide a good description of the observed data; whereas the aliphatic data are typically comprised of larger and more diverse sets of species. Additional rate coefficients would therefore be highly valuable for further assessment and evaluation of the SAR for a variety of aromatic oxygenated species."

Technical corrections:

Equation 4: The product sign between the two terms in the summation argument looks more like a decimal point. I suggest removing it entirely.

Response: We agree with the referee's suggestion and have removed points in equations throughout the revised manuscript.

B. Comments by Luc Vereecken (commenter)

Opening comment:

This is an excellent paper, summarizing many aspects of aromatic chemistry. I will not comment on most of it, as I generally agree with how the analysis is done. Aromatic chemistry is very complex, and the authors are the first to propose useable SARs that capture rate coefficient and site-specificity trends.

Response: We are very grateful to Luc Vereecken for these very positive and supportive comments on our work, and for submitting a detailed and informative discussion comment.

There is, however, one aspect I feel is not in agreement with the experimental observations and the theoretical data available. In particular, I have reservations on a mechanism that incorporates the chemically activated "peroxide-bicyclic" radical (**BCP-yl** in figure LV-1) as an important source of up to 30% of the products. My reasoning is described below in several parts; it is obviously based on incomplete data and thus by no means final. Many of my remarks are based on my recent overview of theoretical studies on aromatic chemistry, of which the authors have received a copy (though much too late to incorporate that data in the paper discussed here). I have summarized the chemical mechanism in figure LV-1 below, and will use the naming and reaction labels in that figure.

I recognize that the proposed mechanism (Figure 3 and 4 in Jenkin et al. 2018) is only a small part of the paper, and this comment is thus not a major criticism of that work. My worry is mainly that no systematic mechanistic improvement can be done by updating rate coefficients and yields of elementary reactions, if the mechanism in the model does not match the underlying chemical process. Given that this mechanism would be implemented in the MCM, the most commonly used semi-explicit mechanism, this could hamper progress significantly. This comment is not as complete as I wanted it to be and may contain errors, as I ran out of time trying to meet the deadline for comment submission. I apologize for the poor presentation of this text and the lack of a more thorough numerical analysis, and remain available to clarify this text.

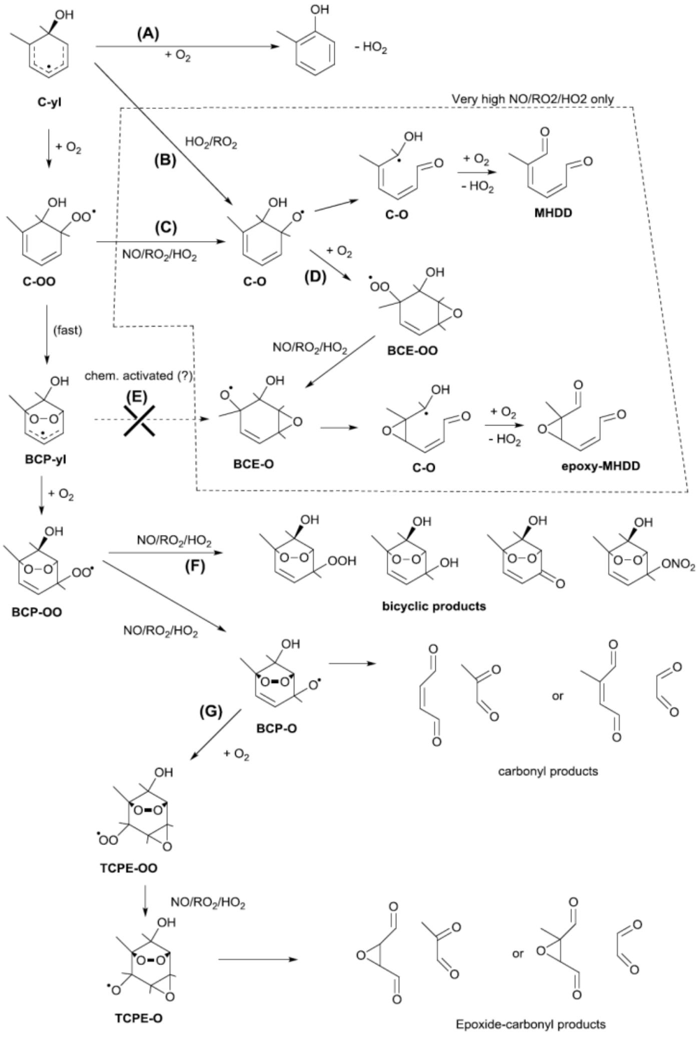

Figure LV-1 : Extended mechanism for aromatic oxidation (toluene used as example). Stereo- and site-specificity is ignored.

Response: We agree that the commenter has raised an area of particular uncertainty in understanding, and welcome this detailed feedback and discussion to allow this to be further highlighted and emphasised. Following careful consideration of the subsequent comments, and the information in the cited literature, we have decided to leave our method unchanged at the present time (as discussed and justified further below). However, we have given additional emphasis to this area of uncertainty in the revised manuscript, including reference to the commenter's discussion comment and to his highly informative forthcoming review of theoretical studies on aromatic oxidation. We would like to emphasise that we have not dismissed the commenter's concerns lightly, and recognise the validity of those concerns, and the insight that has gone into the mechanistic interpretation he has put forward. We hope that advances in understanding will soon allow the various issues discussed below to be reconciled.

We also recognise the commenter's point about processes becoming "hard-wired" into the MCM, and agree that updating the mechanism efficiently has been challenging in the past. A main aim of the current move to automated mechanism construction is to allow updates in understanding to be implemented into the mechanism more readily and efficiently.

a) Chemical activation for BCP-yl.

While it is clear that the nascent **BCP-yl** must have a high internal energy, there is no evidence that it reacts chemically activated to any significant extent, and to me seems unlikely that 30% of the **BCP-yl** will isomerise promptly to epoxy-oxy radicals (**BCE-O**) even for the smallest aromatics.

Prompt decomposition of intermediates in aromatic oxidation, or the pressure dependence of the aromatic oxidation has been studied by several authors ((Glowacki et al., 2009; Lay et al., 1996; Mehta et al., 2009; Pan and Wang, 2015; Wu et al., 2014). Under atmospheric conditions, i.e. around 1 atm. of pressure and air as a bath gas, these studies consistently find that prompt decomposition (channel **E**) has no significant yield. For benzene, Glowacki et al. find at most a few % of prompt decomposition of **BCP-yl** to **BCE-O**, and increasing this yield to 30% would require strong modifications of the kinetic model, likely beyond the reasonable error limits of the applied theoretical methodology. Substituted aromatics have an even higher number of degrees of freedom to redistribute essentially the same nascent excess energy, such that high prompt isomerisation yields of **BCE-O** become even less likely for the more substituted aromatics in the atmosphere. There is no evidence of lower epoxide formation for more substituted aromatics ((Birdsall and Elrod, 2011), which argues against epoxide formation from chemically activated reactions.

In this, one should account for the fact that the theoretical studies such as Glowacki et al. did not consider the bath gas as a reactive collider, i.e. their already low yields of prompt **BCE-O** formation do not account for the near-barrierless addition of O_2 (1/5th of the bath gas collisions), onto **BCP-yl**, forming **BCP-OO** peroxy radicals prior to thermalization, and thus further reducing the yield of BCE-O. One could argue that the energized **BCP-OO** would also be more likely to redissociate, but there will always be sufficient time for energy randomization, such that the leaving O_2 fragment (and the degrees of freedom for relative motion of the fragments) would remove above-thermal energies from **BCP-yl**, leading to even more efficient collisional cooling of the activated **BCP-yl**, and hence smaller contributions of ring opening than the already small predicted yields.

All theoretical calculations indicate that the barrier for peroxide-ring breaking in **BCP-yl** has high barriers across all substituent patterns of aromatics, and the low contribution of prompt ring opening thus appears to hold for all aromatics ((Fan and Zhang, 2006, 2008; Glowacki et al., 2009; Huang et al., 2008, 2010; Li and Wang, 2014; Pan and Wang, 2014, 2015; Suh et al., 2003; Wang, 2015; Wu et al., 2014; Xu and Wang, 2013).

Response: We agree that the 30% proportion we assign to decomposition of BCP-yl is higher than that reported for atmospheric pressure in theoretical studies, and this point was made in the manuscript – although not as clearly as it could have been. We have therefore further emphasised this in the revised manuscript, with reference to the commenter's discussion comment and to his forthcoming review. The relevant text in the manuscript has been modified to read as follows (revised/new text in red font):

> "Inclusion of the "epoxy-oxy" route with this optimized branching ratio results in total prompt HO_2 yields which provide a good representation of those reported by Nehr et al. (2011; 2012), and also the total yields of the well-established α-dicarbonyl products (formed from the alternative O_2 addition chemistry) that are consistent with those reported (see below). However, it is noted that this is an area of significant uncertainty, with theoretical studies predicting a much lower importance of the "epoxy-oxy" route at atmospheric pressure than applied here (e.g. Vereecken, 2018a; 2018b; and references therein). Further studies are required to elucidate the sources of epoxydicarbonylenes and prompt HO_2 in aromatic systems."

As indicated in the manuscript, and discussed further below, the figure of 30 % was empirically optimised on the basis of reported yields of a variety of products (particularly α-dicarbonyls and prompt HO_2) for a series of aromatic hydrocarbons, with evidence for formation of the epoxydicarbonylene products (e.g. epoxy-MHDD in Fig. LV1) formed from BCP-yl decomposition being reported in a number of experimental studies (as cited). In our opinion, a significant reduction in this proportion would result in the mechanism failing to reproduce quantitatively the majority of reported experimental observations. While we accept that this does not prove that the assignment of 30 % to this specific process is correct, the use of a reaction for which there is at least some experimental (and indeed theoretical) support is considered an acceptable interim measure until alternative quantitative explanations are available that do not degrade other aspects of the mechanism's performance.

To illustrate this, Fig. R1 below shows a correlation of calculated and observed yields of the relevant species (a) with the optimised branching ratio of 30 % assigned to BCP-yl decomposition (i.e. as in Fig. 5 of the manuscript); and (b) with a branching ratio of 0 % assigned to BCP-yl decomposition:

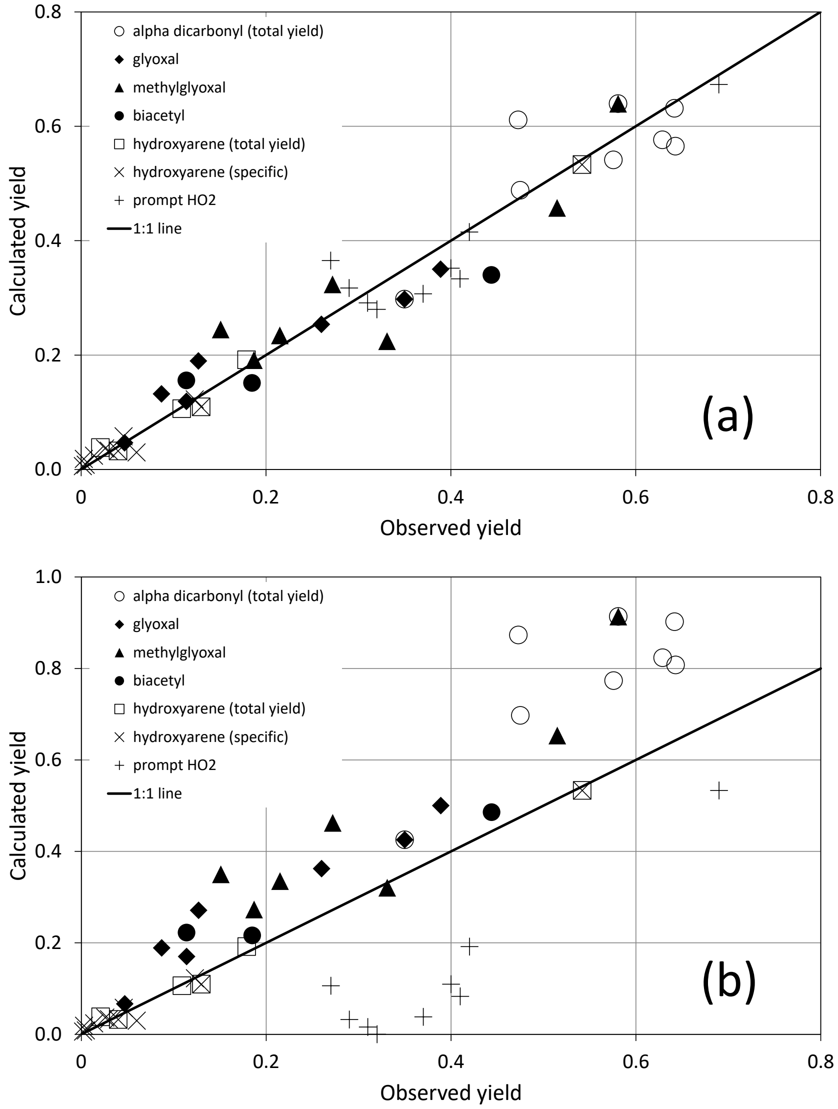

Figure R1: Correlation of calculated and observed yields of hydroxyarenes (total and specific), α-dicarbonyls (total and specific) and prompt HO_2, formed from the degradation of benzene and methyl-substituted aromatic hydrocarbons. Observed data as summarized in Tables S1 and S2. Calculated yields based on (a) optimised method with 30 % decomposition "peroxide bicyclic" intermediates; and (b) with 0 % decomposition "peroxide bicyclic" intermediates.

b) Epoxide formation

The main reason the authors invoke prompt decomposition of **BCP-yl** to **BCE-O** appears to be formation of epoxides, observed in sizable yields by (Baltaretu et al., 2009; Birdsall and Elrod, 2011; Birdsall et al., 2010; Yu and Jeffries, 1997). The authors also list "Kwok et al. 1997", but this is not available in the reference list. It should be noted that Yu and Jeffries also discuss epoxides that only retain part of the carbon skeleton of the aromatic, a pathway that is not available in the mechanism proposed in the Jenkin et al. paper; channels are included in figure LV-1.

Response: As indicated in the previous response, the decomposition of BCP-yl (leading to formation of epoxy-MHDD and analogous products) was invoked for a variety of reasons. The observation of epoxy-MHDD in the experimental studies cited by the commenter provides some support for representing this process, but is not the sole or main reason. We apologise for the omission of the Kwok et al. (1997) reference, and thank the commenter for alerting us to this. This has been corrected in the revised manuscript, and appears as follows:

> “Kwok, E. S. C., Aschmann, S. M., Atkinson, R. and Arey, J.: Products of the gas-phase reactions of o-, m- and p-xylene with the OH radical in the presence and absence of NOx, J. Chem. Soc., Faraday Trans., 93(16), 2847-2854, 1997.”

That study reports formation of the relevant C_8 epoxydicarbonylene products from the xylene isomers.

The authors also mention "prompt HO_2" formation as put to evidence in the work of (Nehr et al., 2011, 2012, 2014). However, this formation does not imply chemically activated reactions nor formation of **BCP-yl** or **BCE-O**, merely NO-free formation of HO_2, for which there are multiple channels available, in particular the H-abstraction by O_2 from the OH-arom adduct, and addition-HO_2 elimination in the first peroxy radicals (indicated as channel **A** in the figure). These channels are also responsible for the formation of (multi-) hydroxylated aromatic products as seen in significant, even high yields for many aromatics, e.g. phenol from benzene, cresols from toluene, and series of multi-hydroxylated aromatics in e.g. (Olariu et al., 2013; Schwantes et al., 2017). This "prompt HO_2" formation is therefore not relevant to this discussion.

Response: We feel the commenter is unreasonably dismissive of the reported observations of prompt HO_2 formation by Nehr et al., which are highly relevant and important. The observation of prompt HO_2 is not “merely NO-free formation of HO_2”, as stated by the commenter, but prompt NO-free formation of HO_2, i.e. not delayed formation that first requires RO_2 to RO conversion via an RO_2 + RO_2 reaction. We consider this a very important feature that has to be represented quantitatively. In very simple terms, the initial step in the mechanism can be represented as follows, with the yield of prompt HO_2 being “α”:

$$\begin{aligned} \text{OH + aromatic } (+\, n\text{O}_2) \quad &\rightarrow \text{HO}_2 + \text{product(s)} \qquad (\alpha) \\ &\rightarrow \text{RO}_2 \qquad\qquad\qquad\quad (1-\alpha) \end{aligned}$$

If we are unable to represent the value of “α” correctly, we have failed at the first step.

The only prompt source of HO_2 mentioned by the commenter above, and presented in Fig. LV1 (other than route E), is its formation in conjunction with hydroxyarene (phenolic) products (in that case cresols), which can occur by two mechanisms that have the same overall chemistry (i.e. that of route A, in Fig. LV1). This well-established process is fully discussed and represented in our work (Sect. 4.1 and Fig. 3). The important point, apparently overlooked by the commenter, is that the reported yields of prompt HO_2 consistently significantly exceed those of the hydroxyarenes. In the case of toluene, for example, the observed total cresol yield from channel A in Fig. LV1, is (17.9 ± 1.6) % (see Table S1), whereas that of prompt HO_2 (i.e. “α”) is (42 ± 11) % (Nehr et al., 2012; Table S2), clearly pointing to a significant missing source. All the other sources of HO_2 presented in Fig. LV1 first require at least one RO_2 to RO conversion and cannot explain this. Again, this does not prove that the excess prompt HO_2 is formed in conjunction with epoxy-MHDD via route E (Fig. LV1). In our opinion, however, that assumption is currently considered more justifiable than increasing the branching ratio of route A (Fig. LV1) to 42 %.

It should be noted that the discrepancy in some other aromatic systems is much greater; e.g. 1,3,5-trimethylbenzene for which the reported hydroxyarene and prompt HO_2 yields are (4 ± 1) % and (29 ± 8) % respectively (see Tables S1 and S2). The use 30 % BCP-yl decomposition appears to resolve the discrepancy acceptably in all aromatic hydrocarbon systems for which yields of hydroxyarene and prompt HO_2 have been reported (see Fig. R1). We are not aware of experimental or theoretical evidence currently supporting any other route that forms prompt HO_2 during OH-initiated aromatic oxidation.

In view of the referee’s comment we have now included a definition of “prompt HO_2” in the relevant discussion of the “epoxy-oxy” route in Sect. 4.1, as follows:

> “As indicated above, the subsequent chemistry leads to prompt formation of HO_2 (i.e. not delayed by first requiring conversion of an organic peroxy radical to an oxy radical via a bimolecular reaction), which supplements that formed in conjunction with the hydroxyarene (phenolic) products (see Fig. 3).”

(Birdsall and Elrod, 2011), figure 7, shows comparable experimental epoxide yields for increasingly substituted aromatics. If epoxide formation occurred through a chemically activated **BCP-yl** reaction, its yield should decrease for larger molecules, given the comparable energy release in **BCP-yl** formation, and the very strongly increased state density in **BCP-yl** upon increasing methylation which slows down prompt decomposition. The TS for ring opening is high in energy, and thus benefits much less from this increase in degrees of freedom at the nascent energies.

Theoretical studies have proposed an alternative route to epoxides (channels **D** and **G** in the figure) that does not require ring breaking in **BCP-yl**, but rather relies on epoxidation of β-unsaturated alkoxy radicals, a reversible process that is captured by O_2 addition on the resulting alkyl radical ((Frankcombe and Smith, 2007; Motta et al., 2002; Pan and Wang, 2014, 2015; Wang, 2015; Wang et al., 2013). These theoretical studies are of course subject to their own uncertainty, but this does provide an explanation that is compatible with the theoretically predicted lack of prompt formation of **BCE-O**. At this time, I will not expand on the accuracy of the theoretical predictions, but rather discuss my interpretation of the experimental evidence below.

Response: We respect the commenter's informed views on the theoretical studies, and note the alternative routes D and G presented in Fig. LV1. Regarding route G, our presented methodology does not rule out formation of the smaller epoxydicarbonyls, as the empirical optimisation is partly based on formation of its α-dicarbonyl co-products, which are formed by both this route and with unsaturated dicarbonyls via the alternative traditional route from BCP-O (see Fig. 4). However, we note that (in the presence of NO_x) route G requires an additional NO-to-NO_2 conversion prior to product formation. This would therefore likely further worsen the common problem encountered in interpreting chamber photo-oxidation of aromatic hydrocarbon/NO_x mixtures, where mechanisms (including the MCM) overestimate initial formation of ozone while underestimating the loss of the aromatic (e.g. Bloss et al., 2005).

c) Experimental data on epoxide formation

A first observation is that all experimental data (Baltaretu et al., 2009; Birdsall et al., 2010; Birdsall and Elrod, 2011; Yu et al., 1997; Yu and Jeffries, 1997) showing epoxide formation were performed at high NO concentrations ranging from 0.8E12 to 2E14molecule cm-3, much higher than atmospherically relevant concentrations. Birdsall and Elrod 2011. also have low-NO experiments, but these appear to have very high RO2 concentration (see below). This changes the chemistry of the aromatic RO_2 intermediates.

Response: We agree with the commenter's observation that experimental studies are sometimes carried out under conditions that are not fully atmospherically relevant (also often acknowledged by the authors of those studies), and that this needs to be taken into account when interpreting results for use in atmospheric mechanisms. We have aimed to do this throughout our work, and have ourselves previously commented on instances where we believe caution is required in transferring experimental results on aromatic oxidation directly into atmospheric mechanisms (e.g. Jenkin et al., 2009; Newland et al., 2017).

The smoking gun in the Birdsall experiments is not necessarily the observation of epoxides, but of methylhexadienedial (**MHDD**) and "bicyclic" products (bicyclic carbonyl, bicyclic alcohol, bicyclic hydroperoxide, and bicyclic nitrate).

The measurable formation of "bicyclic" products, formed in the ketone-alcohol, nitrate, and hydroperoxide channels of **BCP-OO**+NO/HO_2/RO_2 reactions (**F** in our figure, with yields indicated in e.g. figure 4 and 5 in Birdsall et al. 2010) indicates that RO_2 concentrations are high enough to compete with the NO reaction even at NO of concentrations of 1E13 molecule cm-3. The yields of "bicyclic" is slowly decreasing at increasing NO concentrations, as expected. In the low-NO experiments, where "bicyclic" products are highest, there is thus enough RO_2 available for RO_2+RO_2 reactions, and thus also to form a sizable yield of RO radicals. Through all Birdsall experiments, one thus has measurable RO_2 to RO conversion either by RO_2 or NO.

It is hard to imagine a formation pathway for methylhexadienedial (**MHDD**) that does not proceed through hydroxy-methylcyclohexadienoxy (**C-O**). Birdsall et al. 2010 and Birdsall and Elrod 2011 observe this product at high NO concentrations, where this alkoxy radical is likely formed from **C-OO** + NO reactions (pathway **C**). But: they also observed **MHDD** at low NO concentrations, where the **C-O** alkoxy radical can be formed in the alkoxy channel of **C-OO** + RO_2 reactions (pathway **C**), or in the RO_2/HO_2 reactions of the **C-yl** adduct (pahtway **B**, see also figure 2 in Birdsall and Elrod 2011). More **MHDD**, and less "bicyclic" products are formed with increasing NO concentrations (e.g. fig 5, Birdsall et al), indicating a higher **C-OO** to **C-O** conversion with increasing NO, as expected.

<u>Response</u>: We agree with all the above points. The formation of MHDD is likely indicative of conversion of either C-OO or C-yl to C-O, as we also argued in Jenkin et al. (2009).

The O_2-dependence of the **MHDD** yield in NO-free conditions (fig. 5, Birdsall and Elrod 2011) suggests that both the **C-yl** + RO_2 and **C-OO** + RO_2 pathways (**B** and **C**) are forming **C-O**, with **MHDD** yield decreasing from 47% to 15% with increasing O_2 concentrations up to $[O_2]$ ~ 2E18 cm-3 due to increasing competition of O_2 addition on **C-yl**, forming **C-OO** and then **BCP-yl**. At even higher [O2], the yield of **MHDD** is mostly O_2-independent, suggesting the remaining **MHDD** fraction is formed in those conditions is through RO2-based chemistry "**C**" of **C-OO**. This is corroborated by the O_2-dependence of the yield of "bicyclic" products from **BCP-OO** + RO_2 chemistry, which increases strongly up to that same [O2] concentration and remains constant thereafter, i.e. **C-yl** + O_2 is completed, and channel **C** is in steady-state competition with ring closure forming **BCP-yl**. For the purpose of this comment, it is critical mostly that **MHDD** is observed, and that no reasonable formation pathway other than through **C-O** radicals seems to exist. This because the ring closure in **C-OO** forming **BCP-yl** is known to be fast (upper limit ~10^3 s^{-1} experimentally (Bohn, 2001; Bohn and Zetzsch, 1999)), and one would not allow for formation of **C-O** without this experimental proof.

Once **C-O** is formed, its epoxidation reaction **D** can form epoxides, provided the epoxy-alkyl radical is captured by an O_2 addition. The resulting alkylperoxy radical then reacts with NO/RO2/HO2 to form the corresponding alkoxy radical, which is none other than **BCE-O** as formally formed from chemically activated **BCP-yl** ring opening reaction **E**. This **BCE-O** then leads readily to the **epoxy-MHDD** compound after ring breaking and reaction with O_2, as already indicated in the Jenkin et al. paper. The formation of epoxy-products can thus be explained in a manner consistent with the theoretical data, i.e. without prompt ring opening, where the experimental **MHDD** observation is the proof that the high-radical-concentration channels needed to form the intermediate **C-O** are indeed active. **This C-O** formation implies sufficiently high NO/RO2/HO2 concentrations to also convert **BCE-OO** to **BCE-O**.

The O2-dependence of the product yields (figure 4 in Birdsall et all 2010 ; figure 5 in birdsall and Elrod 2011) constitute, in my opinion, experimental proof supplementing the theoretical data that the reaction proceeds by the aforementioned alkoxy radical epoxidation reactions (reversible unless captured by O2), and not by prompt **BCP** ring opening.

As the epoxidation reaction through pathway **D** (and analogously **G**) is reversible and requires a subsequent capturing reaction (typically O_2, though one could envision reactions as in pathways **B**), the ratio of **MHDD** to **epoxy-MHDD** should be dependent on the ratio of the epoxide capturing reaction versus the decomposition of **C-O**. The O_2-dependence shown in figure 4/5 of Birdsall shows that the **epoxy-MHDD**:**MHDD** ratio is indeed much lower at lower O_2, and reaches a constant ratio after $[O_2]$ = ~2E18 cm-3 where the capturing by O_2 of the epoxide has reached saturation and the ratio is thus determined by the ratio of the rates of alkoxy epoxidation versus β-bond scission. The metric is the ratio, not the absolute yield of epoxides, i.e. the absolute epoxide yield could be decreasing or increasing depending on the relative change of increasing epoxide capturing efficiency by O_2, versus lowering **C-O** formation by **C-yl** to **C-OO** capturing by O_2. The epoxide yield is found to be nearly constant or slightly decreasing (from 13% to 10% with increasing O_2 in figure 5 (2011), mostly constant except at very low O_2 in figure 4 (2010)). The O_2-dependence is thus consistent with alkoxy radical epoxidation.

On the other hand, the O_2-dependence of the products appears not consistent with a mechanism based on prompt **BCP-yl** ring opening. The O_2-dependence in figure 4/5 (Birdsall) shows a strongly increasing yield of bicyclic products and (methyl)butenedial with increasing O_2-concentration. This is due to a higher fraction of **C-yl** and **BCP-yl** reacting with O_2, forming more **BCP-OO**. This implies a higher mass flux of chemically activated **BCP-yl***, and thus implies a correlated increase of epoxides if these are formed from prompt ring opening in **BCP-yl**, but this epoxide yield increase is not seen at all. One could (?) argue that the increased formation of chemically activated **BCP-yl** is serendipitously compensated for by an increased collisional deactivation rate which is independent of pressure but only on bath gas composition. This might e.g. occur by the reactive collisions with O_2 acting as "super-collisions", as mentioned in an earlier section. However, figure 4/5 (Birdsall) shows epoxide formation even at very low O_2 concentrations which, if formed from **BCP-yl***, implies a reaction flux through BCP-yl. But all non-epoxide products formed from **BCP-yl** (bicyclic, (methyl)butenedial) have very low yields at very low O_2 in those figures. This is only possible if (a) virtually all **BCP-yl** formed would decompose promptly, (b) that collisional deactivation of **BCP-yl*** would be for the most part done by O_2 and not the other bath gas molecules, (c) that this collisional deactivation would level off at a certain O_2 concentration, with (d) all of this occurring as a function of $[O_2]$ in a very delicate balance against the other rate coefficients. I struggle to accept such serendipity, compared to the more chemically realistic alkoxy epoxidation mechanism in the previous paragraph.

Response: The commenter has focused on the $[O_2]$ dependence of the product yields reported in Fig. 4 of Birdsall et al. (2010) and Fig. 5 of Birdsall and Elrod (2011). These figures show relative yields for the toluene and *o*-xylene systems, and allow the yield of one product relative to another to be judged as a function of conditions. As indicated above, we agree that the $[O_2]$ dependence shown for MHDD (and analogous products), denoted “methylhexadienedial” or “hexadienedial” is consistent with operation of the C-yl + C-OO and C-OO + C-OO pathways. We also agree that the relative $[O_2]$ dependence of MHDD (and analogous products) relative to epoxy-MHDD (and analogous products), denoted “epoxide”, can provide support for the operation of route D (Fig. LV1). However, Fig. 4 of Birdsall et al. (2010) and Fig. 5 of Birdsall and Elrod (2011) also show that formation of BCP-OO related products (denoted “bicyclic”) relative to epoxy-MHDD increases with increasing $[O_2]$. It can therefore also be argued that this supports a competition between decomposition of BCP-yl to BCE-O (via route E) and reaction of BCP-yl with O_2 to form BCP-OO, which is not inconsistent with our representation. The observation of epoxy-MHDD at low $[O_2]$ does not uniquely confirm route D because both routes require sufficient O_2 to be present for initial formation of C-OO. Route D then requires C-OO + C-yl or C-OO + C-OO to occur, whereas route E only requires rapid ring closure to form BCP-yl.

Furthermore, consideration of Fig. 5 of Birdsall et al. (2010), showing the relative yields for the toluene system as a function of [NO], also lend some support to route E. This figure shows that the yield of MHDD increases with increasing [NO] (as expected), but that both epoxy-MHDD and BCP-OO decrease with increasing [NO]. This suggests that epoxy-MHDD and BCP-OO are both formed from a common branch of the chemistry, with MHDD formed from a different and distinct branch – consistent with our representation. We acknowledge, however, that the corresponding relative yield dependence is not as obvious for the o-xylene system in Fig. 6 of Birdsall and Elrod (2011).

In practice, it is therefore probable that both routes D and E are able to operate under appropriate conditions, but with only route E being applicable to atmospheric conditions.

Summary of the argumentation, and some implications.

The main points of my argumentation are then:

a) The observed formation of **MHDD** implies formation of **C-O** intermediates through reactions only accessible in high $RO_2/HO_2/NO$ concentrations.

b) **Epoxy-MHDD** is a companion product of **MHDD** through alkoxy radical epoxidation. The experimental yields as a function of the reaction conditions are consistent with this mechanism. The theoretical data also supports this mechanism

c) Chemically activated ring opening in **BCP-yl** is not supported by any theoretical calculation, nor is there experimental evidence of this. The experimental data on formation of epoxides from **BCP-yl** ring opening as a function of the reaction conditions is not consistent with this mechanism.

The following caveats apply:

a) Only 4 experimental studies are known to me that have observed epoxides; all of these were done in high radical concentrations.

b) The interpretation draws on a rather limited experimental data set, and could easily be an over-interpretation of the data when experimental uncertainties and other factors are taken into account. This is exacerbated by my theoretical background, which makes me less familiar with the limitations and strengths of the experimental data set.

c) The uncertainties on the theoretical data are sizable due to the computational expense of applying the most reliable methodologies on these molecules. Only higher-level calculations can ascertain that the current theoretical predictions are robust.

d) To my knowledge, no kinetic model is available with which the hypotheses can be tested. There is very little experimental data available for such testing.

Response: We are grateful to the commenter for summarising and clarifying these points. We have nothing further to add in relation to the first set of points. We recognise the validity of the commenter suggestions, and agree that further experimental and theoretical studies targeting these issues would be extremely valuable.

Some numerical estimates

The formation of "bicyclic" products (channel **F**) indicates that RO_2 concentrations are high enough to compete with the NO reaction of **BCP-OO** even at NO of concentrations of 1E13 molecule cm^{-3}. The RO_2+RO_2 rate coefficient for allyl-peroxy radicals was measured at 7×10^{-13} cm^3 s^{-1} ((Jenkin et al., 1993), with rate coefficients for other RO_2 radicals + NO lower than this (Orlando and Tyndall, 2012). With a **BCP-OO**+NO rate coefficient of 7.7E-12 cm^3 s^{-1} (Elrod, 2011) we then obtain [RO2] ~ 10^{13} to 10^{14} cm^{-3}.

The **C-OO** to **BCP-yl** ring closure has an experimental upper limit of about 10^3 s^{-1} (Bohn, 2001; Bohn and Zetzsch, 1999)) Theoretical data is within a few orders of magnitude of this, depending on substitution, site-, and stereo-specificity, but the reliability of this data is not better than an order of magnitude. With $k_{cycl} \leq 10^3$ s-1, and NO concentrations of the order of 10^{12} to 10^{14} cm^{-3} (Baltaretu, Yu and Jeffries, Birdsall et al., Birdsall and Elrod), a 1:1 competition for **C-OO** + NO requires a rate coefficient k(NO) ≥ 10^{-11} to 10^{-9} cm^3 s^{-1}. The rate coefficient for **C-OO** + NO has been determined at 1.4E-11 cm^3 s^{-1} (Bohn and Zetzsch, 1999; Klotz et al., 2002). There are also **C-OO** + RO_2/HO_2 reactions competing against the ring closure. Some **C-O** yield through pathway **C** thus appears possible, though with the above numbers it is not a main product.

Formation of **C-O** through channel **B** could supplement the above, competing against O_2 addition. The rate coefficient for **C-yl** + O_2 has been determined at ~10^{-13} to 10^{-16} cm^3 s^{-1} (table 9 in review chapter, Vereecken), comparatively slow due to the loss of resonance stabilization and reduced efficiency by O_2-addition/re-dissociation. Using the experimental value by (Bohn, 2001), 3×10^{-15} cm^3 s^{-1}, and [O_2] from 5E17 to 6E18 cm^{-3} as in Birdsall et al. 2010 yields a pseudo-first order k_{O2} ~ 10^3 to 10^4 s^{-1}. The **C-yl** + RO_2/HO_2 reaction could be more efficient than O_2 addition, as instead of reversing back to **C-yl** + RO_2/HO_2 it could instead break the weak OO bond in the **C-OOR** product. Either way, at least [RO_2/HO_2] of 10^{12} cm^{-3} is needed for it to be physically possible to yield **C-O** (rate coefficient = collision number). Assuming k(**C-yl**+RO_2) = 5×10^{-12} cm^3 s^{-1} then requires [RO_2/HO_2] ~ 10^{14} cm^{-3}, for a 1:1 competition against O_2 addition, or 10^{13} cm^{-3} for 0.1:1 competition, which matches the [RO_2] mentioned above.

Birsall et al. and Birdsall and Elrod also indicate reactions of intermediates with other reaction products (e.g. cresols, see fig 2 in Birdsall et al. 2010/2011). I know of no data that would allow us to estimate these contributions.

Formation of **C-O** thus seems possible in the experimental conditions. The experimental observation of **MHDD** remains a strong argument in favor of **C-O** formation, and its yield does decrease very strongly with increasing [O_2], and increases with increasing NO, in agreement with the proposed mechanism.

Response: We thank the commenter for these estimates. We agree that formation of C-O is possible under some reported experimental conditions, as we also argued in Jenkin et al. (2009).

Proposal of an alternative reduced mechanism

Based on the previous sections and my assessment of the reaction mechanism, I propose an alternative reduced mechanism for aromatics oxidation (see figure LV-2). A first simplification is the observation that formation of **C-O** is only possible in very high RO2/HO2/NO concentrations and/or low O2 concentrations, well beyond the reaction conditions encountered in the atmosphere. Formation of **MHDD**, **epoxy-MHDD**, and other large epoxides are thus unlikely to occur in the atmosphere. I do retain epoxide formation, but only from **BCP-O**, i.e. as companion products of butanedial and other carbonyl products formed after backbone fragmentation. NO-free HO2 formation (labeled "prompt HO2" formation by Nehr et al.) is by H-abstraction or O2-addition/HO2 elimination from the C-yl adduct. Stereospecificity and site-specificity must be ignored or lumped, as otherwise the mechanism becomes unwieldy. However, this implies that most of the reactions in the scheme are not elementary reactions, and their rate coefficients are combinations of several rate coefficients and thus potentially dependent on reaction conditions. As long as the mechanism is applied only in atmospheric conditions, this simplification is unlikely to be problematic, but in some chamber or laboratory studies this might be more troublesome.

Obviously, one could opt for a hybrid mechanism containing the chemistry in fig. LV-1 / LV-2, and channels forming **MHDD** and **epoxy-MHDD** as in Jenkin et al. 2018, until the issue can be resolved.

Response: We are grateful to the commenter for providing a summary mechanism. We have nothing specific to add further to the points made in the responses given above, but look forward to further discussions on this important topic in the future. Although not crucial to the current paper, we would also welcome the opportunity to discuss further the evidence for the formation of epoxy compounds that are co-products to the α-dicarbonyls (i.e. via route G), and will contact the commenter independently of this discussion.

We reiterate our thanks to Luc Vereecken for providing an interesting and informative contribution to the open discussion.

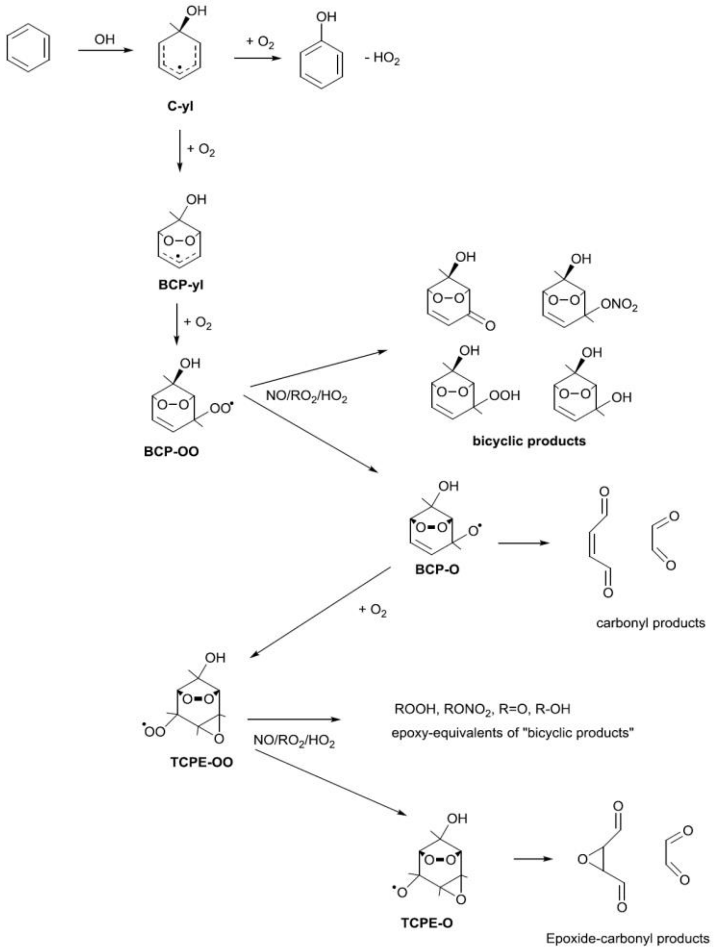

Figure LV-2: Reduced mechanism for aromatic oxidation under atmospheric conditions (stereo- and site-specificity ignored).

[**References**: please see original Discussion comment for Luc Vereecken's reference list]

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