This file contains:

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

  Point-by-point responses to the review comments (original comments are shown in blue font). These responses also include a list of relevant changes made in the manuscript (shown in red font).
- **A marked-up version of the revised manuscript**.

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 $k_{\mathrm{abs(-OH)}}$ (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:
>
> $k_{add} = \Sigma k\, F(\Phi)\, R(\Phi)$ (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.

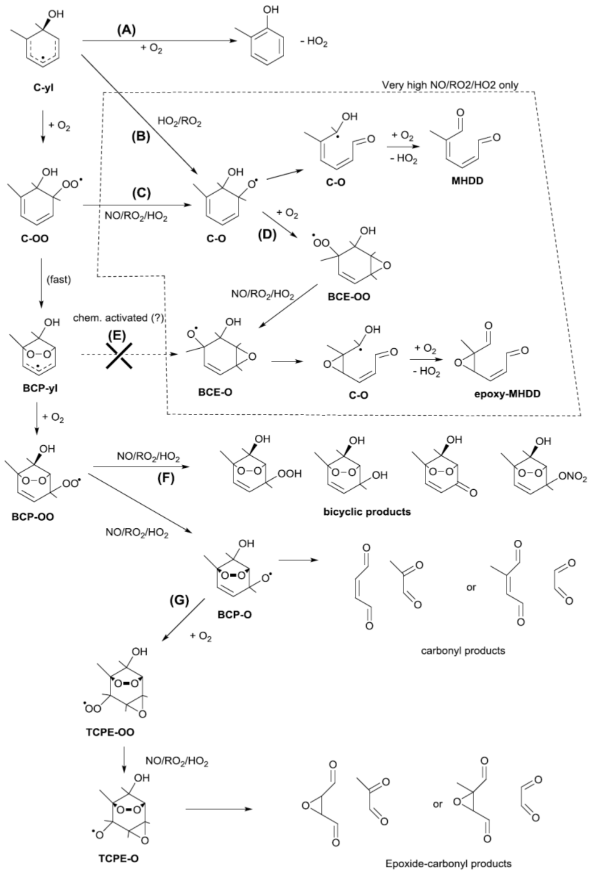

Figure LV-1 : Extended mechanism for aromatic oxidation (toluene used as example). Stereo- and site-specificity is ignored.

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:

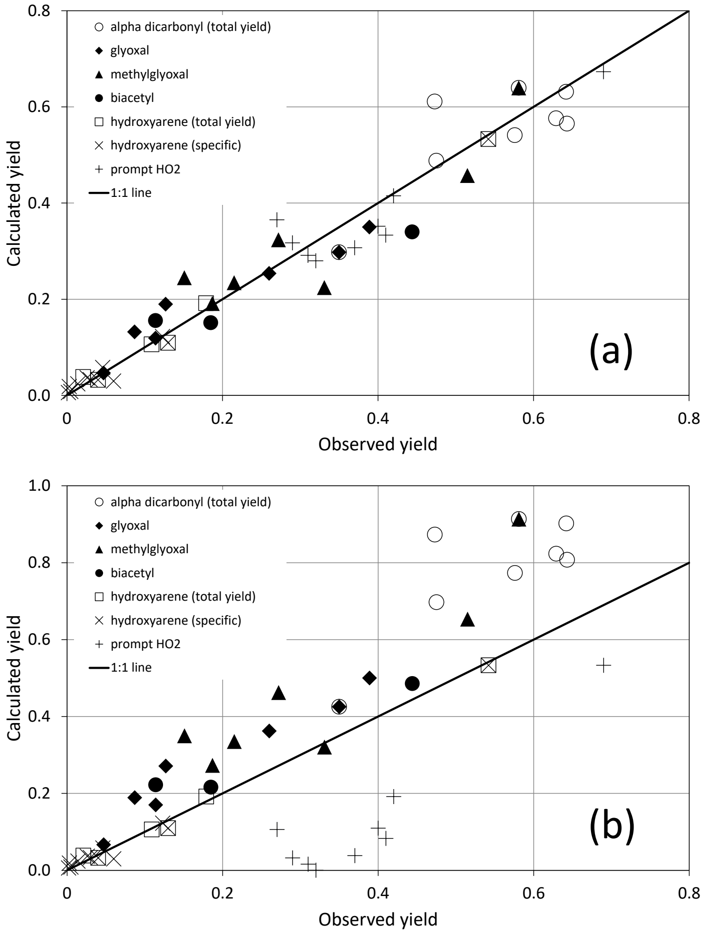

Figure R1: Correlation of calculated and observed yields of hydroxyarenes (total and specific), α-dicarbonyls (total and specific) and prompt HO_2, formed from the degradation of benzene and methyl-substituted aromatic hydrocarbons. Observed data as summarized in Tables S1 and S2. Calculated yields based 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”:

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

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.

Response: 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 $7x10^{-13}$ 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), $3x10^{-15}$ 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) = $5x10^{-12}$ 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.

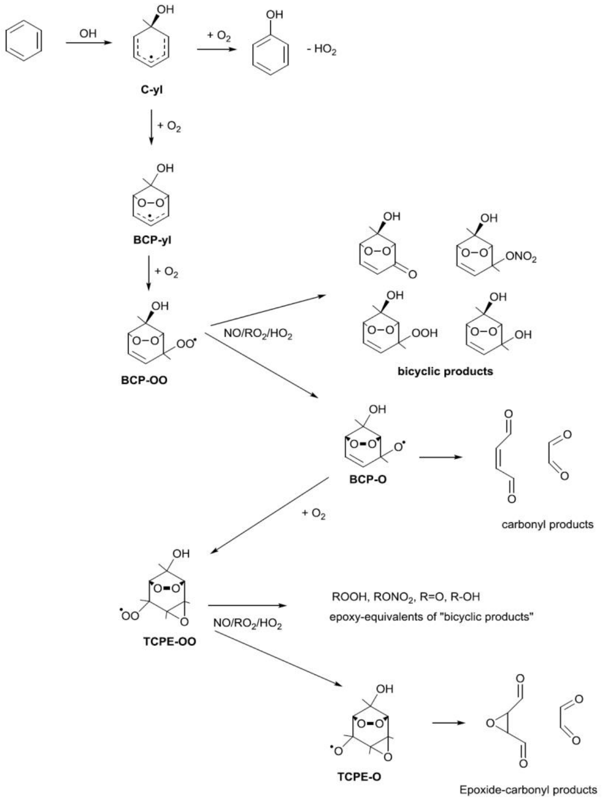

Figure LV-2: Reduced mechanism for aromatic oxidation under atmospheric conditions (stereo- and site-specificity ignored).

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

References not cited in manuscript

Calvert, J. G., Derwent, R. G., Orlando, J. J., Tyndall, G. S. and Wallington, T. J.: Mechanisms of atmospheric oxidation of the alkanes, Oxford University Press, Oxford. ISBN 978-0-19536581-8, 2008.

Calvert, J. G., Mellouki, A., Orlando, J. J., Pilling, M. J. and Wallington, T. J.: The mechanisms of atmospheric oxidation of the oxygenates, Oxford University Press, Oxford. ISBN 978-0-19976707-6, 2011.

Jenkin, M. E., Glowacki, D. R, Rickard, A. R. and Pilling, M. J.: Comment on “Primary Atmospheric Oxidation Mechanism for Toluene”, J. Phys. Chem. A, 113, 8136-8138, 2009.

Newland, M. J., Jenkin, M. E. and Rickard, A. R.: Elucidating the fate of the OH-adduct in toluene oxidation under tropospheric boundary layer conditions, PNAS, 114(38), E7856–E7857, 2017.

Ziemann, P. J. and Atkinson, R: Kinetics, products, and mechanisms of secondary organic aerosol formation, Chem. Soc. Rev., 41, 6582-6605, 2012.

Estimation of rate coefficients and branching ratios for gas-phase reactions of OH with aromatic organic compounds for use in automated mechanism construction

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Abstract. Reaction with the hydroxyl (OH) radical is the dominant removal process for volatile organic compounds (VOCs) in the atmosphere. Rate coefficients for the reactions of OH with VOCs are therefore essential parameters for chemical mechanisms used in chemistry-transport models, and are required more generally for impact assessments involving estimation of atmospheric lifetimes or oxidation rates for VOCs. A structure-activity relationship (SAR) method is presented for the reactions of OH with aromatic organic compounds, with the reactions of aliphatic organic compounds considered in the preceding companion paper. The SAR is optimized using a preferred set of data including reactions of OH with 67 monocyclic aromatic hydrocarbons and oxygenated organic compounds. In each case, the rate coefficient is defined in terms of a summation of partial rate coefficients for H abstraction or OH addition at each relevant site in the given organic compound, so that the attack distribution is defined. The SAR can therefore guide the representation of the OH reactions in the next generation of explicit detailed chemical mechanisms. Rules governing the representation of the reactions of the product radicals under tropospheric conditions are also summarized, specifically the rapid reaction sequences initiated by their reactions with O_2.

1 Introduction

Aromatic hydrocarbons make a significant contribution to anthropogenic emissions of volatile organic compounds (VOCs), representing an important component of vehicle exhaust and other combustion emissions, and evaporative emissions of petroleum and from industrial processes and solvent usage (e.g. Calvert et al., 2002; Passant, 2002). They are also emitted from sources that are either partially or wholly natural. They represent a significant proportion of VOC emissions from biomass burning sources (e.g. Hays et al., 2002; Lewis et al., 2013), and are emitted substantially from vegetation (e.g.

Misztal et al., 2015). An important contributor to these natural emissions is~~ in the form of~~ *p*-cymene (e.g. Helmig et al., 1998; Owen et al., 2001; Maleknia et al., 2007; Ulman et al., 2007), which is also formed as a degradation product of the reactive monoterpenes α-terpinene, α-phellandrene and γ-phellandrene (e.g. Berndt et al., 1996; Peeters et al., 1999; Aschmann et al., 2011). The aromatic oxygenate, methyl chavicol (1-allyl-4-methoxybenzene), has also been reported to be emitted in large quantities from vegetation (Bouvier-Brown et al., 2009; Misztal et al., 2010), with evidence for a number of other aromatic oxygenates also reported (Misztal et al., 2015). It is well established that the gas phase degradation of VOCs in general plays a central role in the generation of a variety of secondary pollutants, including ozone and secondary organic aerosol, SOA (e.g. Haagen-Smit and Fox, 1954; Went, 1960; Andreae and Crutzen, 1997; Jenkin and Clemitshaw, 2000; Hallquist et al., 2009). By virtue of their generally high reactivity and emissions, the oxidation of aromatic compounds is believed to make an important contribution to the formation of ozone on local and regional scales (Derwent et al., 1996; Calvert et al., 2002), and to the formation of SOA in urban areas (e.g. Odum et al., 1997; Genter et al., 2017).

The complete gas-phase oxidation of aromatic hydrocarbons proceeds via highly detailed mechanisms, producing a variety of intermediate oxidized organic products, some of which retain the aromatic ring (e.g. Calvert et al., 2002; Jenkin et al., 2003; Bloss et al., 2005). Reaction with the hydroxyl (OH) radical is generally the dominant or exclusive removal process for aromatic hydrocarbons, and makes a major contribution to the removal of aromatic oxygenates. Quantified rate coefficients for these reactions are therefore essential parameters for chemical mechanisms used in chemistry-transport models, and are required more generally for environmental assessments of their impacts, e.g. to estimate the kinetic component of ozone formation potentials (Jenkin et al., 2017). In addition to the total rate coefficient, quantification of the branching ratio for attack of OH at each site within a given compound is required for explicit representation of the subsequent oxidation pathways in chemical mechanisms.

In the present paper, a structure-activity relationship (SAR) method is presented for the reactions of OH with aromatic organic compounds, with the reactions of aliphatic organic compounds considered in the preceding companion paper (Jenkin et al., 2018a). 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.

The information is currently being used to guide the representation of the OH-initiation reactions in the next generation of explicit detailed chemical 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). It is therefore contributes to a revised and updated set of rules that can be used in automated mechanism construction, and provides formal documentation of the methods. To facilitate this, rules governing the representation of the reactions of the product radicals under tropospheric conditions are also summarized, specifically the rapid reaction sequences initiated by their reactions with O_2. The subsequent chemistry (e.g. reactions of peroxy radicals) will be considered elsewhere (Jenkin et al., 2018b).

2 Preferred kinetic data

A set of preferred kinetic data has been assembled from which to develop and validate the estimation methods for the OH rate coefficients, as described in the companion paper (Jenkin et al., 2018a). The subset relevant to the present paper comprises 298 K data for 25 monocyclic aromatic hydrocarbons (with temperature dependences also defined in 13 cases); and 42 aromatic oxygenated organic compounds (with temperature dependences also defined in 7 cases). In one case (1,2-diacetylbenzene), the preferred rate coefficient is an upper limit value. The information is provided as a part of the Supplement (spreadsheets SI_6 and SI_7). As described in more detail in Sect. 3.2, the oxygenates include compounds containing a variety of oxygenated substituent groups that are prevalent in both emitted VOCs and their degradation products, namely -OH, -C(OH)<, -C(=O)-, -O- , -C(=O)O- and $-NO_2$ groups. For a core set of 11 reactions, the preferred kinetic data are based on the evaluations of the IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation (http://iupac.pole-ether.fr/). The remaining values are informed by recommendations from other key evaluations with complementary coverage (e.g. Atkinson and Arey, 2003; Calvert et al., 2011), and have been revised and expanded following review and evaluation of additional data not included in those studies (as identified in spreadsheets SI_6 and SI_7).

3 Kinetics and branching ratios of initiation reactions

The reaction of OH with a given aromatic compound can occur by both addition of OH to the aromatic ring and by abstraction of an H-atom from a C-H or O-H bond in a substituent group. The estimated rate coefficient is therefore given by $k_{calc} = k_{add} + k_{abs}$, where k_{add} and k_{abs} are summations of the partial rate coefficients for OH addition and H-atom abstraction for each attack position in the given aromatic compound. Based on reported data for the reaction of OH with benzene, abstraction of H-atoms from the aromatic ring itself is assumed to be negligible under atmospheric conditions (e.g. see Calvert et al., 2002).

A method for estimating rate coefficients for OH addition to the aromatic ring (k_{add}), and the distribution of attack, is described in the sections that follow. The estimation of rate coefficients for H-atom abstraction from substituent groups (k_{abs}) follows the methods described in the companion paper (Jenkin et al., 2018a), which are mainly based on updating and extending the widely applied method of Kwok and Atkinson (1995). For C-H bonds, the estimated rate coefficients are thus generally based on a summation of rate coefficients for H-atom abstraction from the primary ($-CH_3$), secondary ($-CH_2-$) and tertiary (-CH<) groups which are calculated as follows:

$$k(CH_3\text{-}X) = k_{prim}\,F(X) \quad (1)$$

$$k(X\text{-}CH_2\text{-}Y) = k_{sec}\,F(X)\,F(Y) \quad (2)$$

$$k(\text{X-CH(-Y)-Z}) = k_{\text{tert}}\,\text{F(X) F(Y) F(Z)} \quad (3)$$

k_{prim}, k_{sec} and k_{tert} are the respective group rate coefficients for abstraction from primary, secondary and tertiary groups for a reference substituent; and F(X), F(Y) and F(Z) are factors that account for the effects of the substituents X, Y and Z. The reference substituent is defined as "-CH_3", such that F(-CH_3) = 1.00 (Atkinson, 1987; Kwok and Atkinson, 1995). As described in detail in the companion paper (Jenkin et al., 2018a), a number of fixed rate coefficients are also defined for H-atom abstraction from O-H bonds in hydroxy, hydroperoxy and carboxyl groups; and for C-H bonds in a series of formyl groups, and adjacent to -O- linkages in ethers. The values of these rate coefficients are assumed to be independent of the identity of neighbouring substituent groups. The methods summarized above are extended in the present work to include rate coefficients and neighbouring group substituent factors for H-atom abstraction from carbon and oxygen atoms adjacent to aromatic rings.

For aromatic compounds containing an unsaturated substituent, the addition of OH to C=C bonds in the substituent group can also occur. The treatment of these reactions is described in Sect. 3.1.3.

3.1 Aromatic hydrocarbons

3.1.1 Methyl-substituted aromatic hydrocarbons

The set of preferred kinetic data contains rate coefficients for the reactions of OH with 12 methyl-substituted aromatic hydrocarbons possessing between one and six methyl substituents. This class is the most comprehensively studied, with room temperature data covering all possible methyl-substituted isomers. Although rate coefficients for this class of compound do not therefore need to be estimated, the SAR described below aims to rationalize the variation of reactivity from one compound to another, and to provide a method of estimating the OH attack distributions that can be applied in automated mechanism generation.

The contribution of H-atom abstraction to the total rate coefficient is known to be minor at temperatures relevant to the atmosphere for methyl-substituted aromatics (e.g. Calvert et al., 2002; Loison et al., 2012; Aschmann et al., 2013). The temperature-dependent reference substituent factor for a phenyl group, F(-Ph1) (see Table 1), was set so that the H-atom abstraction rate coefficient for the methyl group in toluene matches the IUPAC recommendation, i.e. $2.5 \times 10^{-11} \exp(-1270/T)$ $\text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$ (IUPAC, 2017a). The branching ratios reported in the above studies suggest that H-atom abstraction is slightly more efficient for methyl groups in some polymethyl-substituted aromatics, particularly for hexamethylbenzene (Loison et al., 2012), probably reflecting an additional stabilizing effect on the resonant product radical. The data were thus found to be reasonably well described by assigning a further activation factor of exp(140/T) (equating to a value of 1.6 at 298 K) for each additional methyl group positioned *ortho*- or *para*- to the abstraction group. The resultant estimated branching ratios for H-atom abstraction are discussed further below.

The current estimation method defines site-specific parameters for addition of OH to each carbon atom in the aromatic ring. As shown in Table 2, k_{arom} is used to represent addition of OH to an unsubstituted carbon, and k_{ipso} is used to represent addition of

OH to a methyl-substituted carbon. The total rate coefficient for OH addition is then given by a summation of the partial rate coefficients for each of the six attack positions,

$$k_{\text{add}} = \Sigma k\ \text{F}(\Phi) \tag{4}$$

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.

As shown in Table 3, the dataset was described in terms of 11 substituent factors, representing the effects of between one and five methyl substituents. Based on the results of previous assessments (e.g. see Calvert et al., 2002), the number of parameters was limited by assuming that *ortho*- and *para*- substituents have the same influence, whether individually or in combinations. Examples of rate coefficient calculations using these parameters are given in the Supplement.

The values of the F(Φ) factors in Table 3 and k_{ipso} were varied iteratively to minimize the summed square deviation, $\Sigma((k_{\text{calc}}-k_{\text{obs}})/k_{\text{obs}})^2$ at 298 K for the set of methyl-substituted aromatic hydrocarbons. Within the context of previous appraisals (e.g. Calvert et al., 2002 and references therein), the resultant values show some consistent trends, with *ortho*- and *para*- substituents being significantly more activating than *meta*- substituents. It is also interesting to note that the elevation in k_{ipso} relative to k_{arom} (i.e. a factor of 1.4) is identical to the activating influence of a lone *meta*- substituent, which is also consistent with previous assumptions (e.g. Calvert et al., 2002). Increasing the number of substituents has a generally increasing activating impact, although the highest value was returned for F(*o*-,*o*-,*p*-), i.e. for three substituents in the most activating positions, with this value being determined by the observed rate coefficients for 1,3,5-trimethylbenzene and 1,2,3,5-tetramethylbenzene. A correlation of the optimized values of k_{calc} with k_{obs} at 298 K is shown in Fig. 1. The estimation method reproduces all the observed values to within 5 %.

The estimated contributions of H-atom abstraction from the methyl substituents in the series of aromatics hydrocarbons are compared with those reported, in Table 4. The values confirm that rate coefficients assigned to these reactions in Table 1 provide a reasonable description for the complete dataset of methyl-substituted aromatics.

There have been no direct experimental determinations of the branching ratios for OH addition to methyl-substituted aromatic rings, although a number of Density Functional Theory (DFT) studies have been reported for toluene, *m*-xylene, *p*-xylene and 1,2,4-trimethylbenzene (Suh et al., 2002; Fan et al., 2006; 2008; Huang et al., 2011; Wu et al., 2014; Li et al., 2014). As shown in Table 5, the attack distributions of OH predicted by the partial rate coefficients determined from the present method are generally consistent with those reported in the theoretical studies, providing a level of independent support for the method developed here. The distributions for toluene and *p*-xylene are in good agreement with those reported in the DFT studies, with those for 1,2,4-trimethyl benzene also being in reasonable agreement. For *m*-xylene, the major channels (i.e. addition at positions (2) and (3)) are consistent with those reported by Fan et al. (2008) and Huang et al. (2011), although their relative importance is reversed. The present method predicts addition at position (3) to be more important because of its greater degeneracy, whereas the DFT studies predict that this is outweighed by a much stronger activating influence of the two *ortho*- substitutions on position (2) compared with that of the *ortho*- and *para*- substitutions on position (3). Conversely, the opposite appears to be the case for 1,2,4-trimethyl benzene, where the DFT study of Li et al. (2014) calculates position (5) (with *ortho*- and *para*- substitutions) to be favoured over position (4) (with two *ortho*- substitutions), despite both sites being singly degenerate in that case.

Temperature-dependent recommendations are available for benzene and 10 methyl-substituted aromatics in Arrhenius format ($k = A.\exp(-(E/R)/T)$ (see spreadsheet SI_6). These were used to provide optimized temperature coefficients ($B_{F(\Phi)}$) and pre-exponential factors ($A_{F(\Phi)}$) for the set of OH addition substituent factors given in Table 3. Optimization was achieved by calculating values of k at even 1/T intervals over the recommended temperature range for each aromatic, and determining a composite E/R value from a least squares linear regression of the data on an Arrhenius (i.e. ln(k) vs. 1/T) plot. The 11 values of values of $B_{F(\Phi)}$ in Table 3 were varied to minimize the summed square deviation in the composite temperature coefficients, $\Sigma((E/R)_{calc}-(E/R)_{obs})^2$. The resultant $(E/R)_{calc}$ values are compared with the recommended $(E/R)_{obs}$ values in the lower panel of Fig. 1 (see also Fig. S1). The values of $A_{F(\Phi)}$ were automatically returned from the corresponding optimized $B_{F(\Phi)}$ and $F(\Phi)_{298\ K}$ values.

3.1.2 Higher alkyl-substituted aromatic hydrocarbons

The set of preferred kinetic data contains rate coefficients for a further eight alkyl-substituted aromatic hydrocarbons, namely ethylbenzene, *n*-propylbenzene *i*-propylbenzene, *t*-butylbenzene, *o*-ethyltoluene, *m*-ethyltoluene, *p*-ethyltoluene and *p*-cymene. Information on H-atom abstraction from this series of compounds is limited to the study of *p*-cymene (4-*i*-propyltoluene) reported by Aschmann et al. (2010) and Bedjanian et al. (2015), who determined a total branching ratio for H-atom abstraction of about 20 %, with about 15 % from the -CH< group in the *i*-propyl substituent (see Table 4). Use of the aromatic substituent factors appropriate to H-atom abstraction from α -CH_3 groups (i.e. F(-Ph1) in Table 1) would clearly lead to a gross overestimation for *p*-cymene (i.e. about 34 % from the -CH< group in the *i*-propyl substituent and a total of about 39 %), and also unreasonably large contributions in the other compounds identified above. Based on the *p*-cymene data, a substituent factor of 1.0 is assigned to F(-Ph2), representing H-atom abstraction from a substituent α -CH< group, and also applied to abstraction from an α -CH_2- group in ≥ C_2 substituents (see Table 1). As for the -CH_3 groups discussed above, the further activation factor of exp(140/T) (equating to a value of 1.6 at 298 K) is applied for each additional alkyl group positioned *ortho*- or *para*- to the abstraction group. For *p*-cymene, this results an estimated total branching ratio for H-atom abstraction of 22.4 %, with 16.2 % from the -CH< group in the *i*-propyl substituent (see Table 4), in good agreement with the observations of Aschmann et al. (2010) and Bedjanian et al. (2015). It is noted that the value of 1.0 assigned to F(-Ph2) at 298 K is unchanged from that previously reported by Kwok and Atkinson (1995) for phenyl groups in general.

The methyl group substituent factors in Table 3 provide a reasonable first approximation for the effects of the higher alkyl groups on OH addition rate coefficients, and use of those factors leads to a set of estimated rate coefficients that are all within 30 % of the observed values for the current set of eight higher alkyl-substituted aromatic hydrocarbons. On the whole, however, this results in a slight overestimation ~~in~~ of the rate coefficients. 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:

$$k_{add} = \Sigma k\ F(\Phi)\ R(\Phi) \qquad (5)$$

These result in a generally improved agreement, with deviations from the observed rate coefficients of ≤ 16 % (see Fig. 1). For the present set of compounds, these adjustment factors are only defined for the impacts of *ortho*- and *para*- substitutions, as adjustments for *meta*- and *ipso*- groups appeared to result in more subtle benefits. In principle, ~~these adjustments~~a value of R(Φ) should be applied for each higher alkyl group in the molecule, although none of the current set contains more than one higher alkyl substituent. The factors appear to show a deactivating effect (relative to that of methyl) that increases with the size of the alkyl group, with this being qualitatively consistent with information reported in previous appraisals (e.g. see Calvert et al., 2002). It is emphasized, however, that the adjustment factors are derived from the analysis of a very small dataset, with some factors based on reported data for a single compound. Clearly, further systematic kinetic studies of higher alkyl-substituted aromatics would be of benefit.

Similarly to above, there have been no direct experimental determinations of branching ratios for OH addition to higher alkyl-substituted aromatics, although Huang et al. (2010) have reported a DFT study for ethylbenzene, and Alarcón et al. (2014) for *p*-cymene. As shown in Table 5, the attack distributions of OH predicted by the partial rate coefficients determined from the present method agree reasonably well with those reported.

Temperature-dependent studies are only available for *p*-cymene (Alarcón et al., 2014; Bedjanian et al., 2015), resulting in a recommended value of E/R = -640 K. The parameters discussed above are unable to recreate this temperature dependence, and logically return a temperature dependence comparable to that of the structurally similar compound *p*-xylene, for which the recommended E/R = -160 K. It was found that this discrepancy could be resolved by applying a temperature dependent value of $R_{i\text{-pr}}(o\text{-}) = R_{i\text{-pr}}(p\text{-}) = 0.029.\exp(1000/T)$ (see Table 6 comment (d)). This results in *i*-propyl groups becoming more activating relative to methyl groups as the temperature is lowered, with values of $R_{i\text{-pr}}(o\text{-})$ and $R_{i\text{-pr}}(p\text{-}) > 1$ at temperatures below about 280 K. The DFT calculations of Alarcón et al. (2014) provide some support for this trend for $R_{i\text{-pr}}(o\text{-})$. Provisional temperature dependences are also suggested for the other $R_{\text{alkyl}}(o\text{-})$ and $R_{\text{alkyl}}(p\text{-})$ values (see Table 6 comments), although it is again emphasized that these parameters are generally based on very limited information.

3.1.3 Alkenyl-substituted aromatic hydrocarbons

The set of preferred kinetic data contains rate coefficients for the reactions of OH with four alk-1-enyl (or vinyl) substituted aromatic hydrocarbons, namely styrene (ethenylbenzene), α-methylstyrene (*i*-propenylbenzene), β-methylstyrene (propenylbenzene) and β,β-dimethylstyrene (2-methylpropenylbenzene). Experimental and theoretical information for the most studied compound, styrene, is consistent with the reaction occurring predominantly by addition of OH to the ethenyl substituent (Bignozzi et al., 1981; Tuazon et al., 1993; Cho et al., 2014). However, unlike the trends in rate coefficients for aliphatic alkenes (see Sect. 4.1.1 of Jenkin et al., 2018a), the presence of the alkyl substituents on the alkene group in the series of styrenes does not apparently enhance the reactivity, with very similar 298 K rate coefficients reported for styrene, α-methylstyrene and β-methylstyrene, and a reduction in reactivity for the most substituted compound, β,β-dimethylstyrene. A fixed rate coefficient, $k_{\text{C=C-Ph}} = 9.8 \times 10^{-12} \exp(530/T)$ cm^3 molecule^{-1} s^{-1}, is therefore provisionally assigned to addition of OH to alk-1-enyl (vinyl) substituents, based on the preferred value for styrene at 298 K, and the value of E/R calculated by Cho et al. (2014). The reaction is assumed to occur exclusively by addition to the β carbon in the substituent group, because this forms a resonance-stabilized radical. Accordingly, the presence of an alk-1-enyl (vinyl) substituent is assumed to result in complete deactivation of OH addition to the aromatic ring (see Table ~~3~~6).

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.

3.2 Monocyclic aromatic oxygenates

The preferred 298 K data include rate coefficients for reactions of OH with 42 aromatics containing a variety of oxygenated substituent groups, which were used to extend the methods described above for estimating rate coefficients for aromatic hydrocarbons. Rate coefficients for H atom abstraction from the oxygenated groups are generally represented using the methods applied to aliphatic oxygenates (Jenkin et al., 2018a), in conjunction with the values of F(X) given in Table 1, where appropriate; but with specific parameters defined for abstraction from -OH and -C(=O)H substituents (see Sects. 3.2.1 - 3.2.3). For addition of OH to the aromatic ring, the influences of the oxygenated substituents are described by the set of adjustment factors, R(Φ), given in Table 6. As for the higher alkyl substituents discussed in Sect. 3.1.2, these represent corrections to the values of F(Φ) in Table 3, and to k_{ipso} in Table 2, and are applied for each oxygenated substituent in the given molecule. They thus describe the effect of the oxygenated substituent relative to that of a $-CH_3$ group in the same position. In many cases, values of R(Φ) are derived from the analysis of a limited number of compounds containing the relevant substituent, with some based on reported data for a single compound, as summarized in the notes to Table 6. However, the values for -OH, -C(=O)H and $-NO_2$ are based on analysis of larger sets of compounds, as described in following subsections. With the exception of three catechols, the values of R(Φ) in Table 6 are determined from sets of compounds containing only one of the relevant oxygenated substituent. As a result, extrapolation of the method to compounds containing several activating substituents can result in unreasonably high estimated rate coefficients (i.e. exceeding the bimolecular collision rate). An upper limit rate coefficient, $k_{calc} = 3.0 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, is therefore imposed. Further data for aromatics containing multiple oxygenated substituents are clearly required to allow the method to be tested and refined.

3.2.1 Phenols and catechols

The contribution of H-atom abstraction from the -OH substituent in phenolic compounds has generally been inferred from the measured yields of nitrophenolic products, under conditions when the intermediate phenoxy radicals are expected to react predominantly with NO_2. Based on the nitrophenol yields reported for phenol and the set of cresol isomers by Atkinson et al. (1992), Olariu et al. (2002), Berndt and Böge (2003) and Coeur-Tourneur et al. (2006), an average rate coefficient, $k_{abs(Ph-OH)}$ = 2.6

× 10^{-12} cm^3 $molecule^{-1}$ s^{-1}, is assigned to this abstraction reaction at 298 K. This is about a factor of 20 greater than estimated for abstraction from -OH groups in aliphatic compounds (Jenkin et al., 2018a), which can be attributed to the resonance stabilization of the product phenoxy radicals. This suggests that the value of $k_{abs(Ph-OH)}$ may therefore be influenced by the presence of other substituents on the aromatic ring. This cannot be confirmed unambiguously from the reported dataset for phenols and cresols, although the presence of the *ortho*- NO_2 group in 2-nitrophenols appears to have a significant deactivating effect (see Sect. 3.2.3). There is currently insufficient information to allow a full appraisal of the effects of the variety of possible substituents groups on H-atom abstraction from -OH (or other) substituents. In the present work, therefore, the above value of $k_{abs(Ph-OH)}$ is applied, unless the compound contains either an *ortho*- NO_2 group or (by inference) a *para*- NO_2 group. $k_{abs(Ph-OH)}$ is assumed to be independent of temperature over the atmospheric range, which is consistent with the provisional temperature dependence expressions suggested by Atkinson (1989), inferred from extrapolation of higher temperature data for phenol and *o*-cresol.

The values of $R_{OH}(\Phi)$ in Table 6 were varied iteratively to minimize the summed square deviation, $\Sigma((k_{calc}-k_{obs})/k_{obs})^2$ at 298 K for phenol, 14 methyl-substituted phenols, catechol and two methyl-substituted catechols. The resultant values of k_{calc} agree reasonably well with k_{obs} for the complete set of compounds (see ~~upper panel of~~ Fig. 2), with particularly good agreement for the the more substituted phenols and the catechols. Although the agreement is less good for the smaller, less reactive compounds (particularly for phenol, $k_{calc}/k_{obs} \approx 0.6$, and *p*-cresol, $k_{calc}/k_{obs} \approx 0.7$), the values of $R_{OH}(\Phi)$ are considered appropriate for wider application to multifunctional aromatic ~~products~~ compounds containing -OH substituents for which there is currently no information. Temperature dependent data are currently limited to phenol and the cresol isomers. Use of the temperature dependent factors given in Table 6 allows a reasonable representation of observed preferred temperature dependences, as shown in the lower panel of Fig. 2 (see also, Fig. S2).

The attack distributions predicted by the optimized parameters recreate some of the features inferred from reported experimental studies for phenol and cresols (e.g. Olariu et al., 2002), initiating routes to the observed formation of catechols (1,2-dihydroxyarenes), benzoquinones and nitrophenols (see Sect. 4.2). As shown in Table 6, comparable values of $R_{OH}(\Phi)$ for each attack position are required to recreate the observed kinetics for the complete set of phenolic compounds. As a result, the -OH substituent retains the greater *ortho*- and *para*- directing influence discussed above for the reference substituent, $-CH_3$. The optimized parameters therefore predict significant formation of catechols from the oxidation of mono-phenols (resulting from *ortho*- attack), qualitatively consistent with the results of the experimental studies. However, the optimized *ortho*- directing influence of the -OH substituent is still insufficient to recreate the observed dominant (65-80 %) formation of catechol products, reported for phenols and cresols (e.g. Olariu et al., 2002). Noting that the product studies mainly consider the smaller compounds for which the parameter optimization procedure works least well, this may be indicative of the contribution of *ortho*- attack of OH being underestimated for these compounds, but with the method being reasonable for wider application to more substituted aromatic products containing -OH substituents. It is generally recommended that attack distributions (and rate coefficients) based on the results of experimental studies are applied where evaluated information is available, as presented specifically for phenol and the cresol isomers in Sect. S3.

3.2.2 Benzaldehydes

The set of preferred kinetic data contains rate coefficients for benzaldehyde, three methyl-substituted benzaldehydes and six dimethyl-substituted benzaldehydes. In addition, preferred data are included for phthaldialdehyde (1,2-diformylbenzene) and 2-acetylbenzaldehyde, and an upper limit rate coefficient for the related compound 1,2-diacetylbenzene, based on Wang et al. (2006). The data show that the presence of methyl substituents in the benzaldehydes increases the OH reactivity systematically. It is generally accepted that abstraction of the H-atom from the formyl (-C(=O)H) substituent is the dominant pathway for benzaldehyde, and this has been estimated to account for about 96 % of the reaction at 298 K in the DFT study of Iuga et al. (2008). As discussed previously (e.g. Thiault et al., 2002; Clifford et al., 2005; Clifford and Wenger, 2006), the activating effect of the methyl substituents may therefore result from an increasing contribution of OH addition and/or from an activating influence on the abstraction rate from the formyl substituent.

Initially, it was assumed that the rate coefficient for H-atom abstraction from the formyl group, $k_{\mathrm{abs(Ph\text{-}C(O)H)}}$, remains constant for the complete series of compounds. Values of $k_{\mathrm{abs(Ph\text{-}C(O)H),}}$ and of a set of adjustment factors for OH addition, $R_{\mathrm{C(O)H}}(\Phi)$, were varied iteratively to minimize $\Sigma((k_{\mathrm{calc}}\text{-}k_{\mathrm{obs}})/k_{\mathrm{obs}})^2$ at 298 K, leading to a set of parameter values given in Sect. S4 (Table S4). These predict that the contribution of H-atom abstraction from benzaldehyde is 86 %, decreasing to 36–46 % for the dimethylbenzaldehyde isomers. Although this is consistent with a major contribution for benzaldehyde, the predicted value is significantly lower than the 96 % calculated for H-atom abstraction by Iuga et al. (2008). With the reasonable assumption that the values of $R_{\mathrm{C(O)R}}(\Phi)$ for -C(=O)H substituents can also be applied more generally to -C(=O)R substituents, the estimated rate coefficient for 1,2-diacetylbenzene also exceeds the reported upper limit value by more than a factor of two. This suggests that these ~~above~~ optimized parameters also significantly overestimate OH addition to the aromatic ring.

An alternative procedure was therefore adopted in which the contribution of H-atom abstraction from the -C(=O)H group in benzaldehyde was constrained to 96 % at 298 K (providing a reference value of $k_{\mathrm{abs(Ph\text{-}C(O)H)}} = 1.21 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}); and the values of $R_{\mathrm{C(O)H}}(\Phi)$ were varied to reproduce the total rate coefficient for benzaldehyde, leading to the (strongly deactivating) values presented in Table 6. The activating influence of the methyl substituents is then partly accounted for by increases in the OH addition rate coefficients, but also requires H-atom abstraction from the -C(=O)H group to be enhanced. Based on optimization to the complete set of rate coefficients, the data were found to be well described by assigning activation factors of exp(115/T) (equating to a value of 1.47 at 298 K) for a methyl group positioned *ortho*- to the -C(=O)H group group, and exp(78/T) (equating to a value of 1.30 at 298 K) for a methyl group positioned either *meta*- or *para*- to the -C(=O)H group (with these factors also assumed to apply to other alkyl groups). A correlation of the optimized values of k_{calc} with k_{obs} at 298 K is shown in Fig. 2, with the estimation method reproducing all the observed values to within 10 %. Based on this approach, H-atom abstraction from the -C(=O)H group remains the most important route, decreasing from 96 % for benzaldehyde to 76–88 % for the dimethylbenzaldehyde isomers. The optimized parameters also provide a reasonable description of the data for phthaldialdehyde (1,2-diformylbenzene) and 2-acetylbenzaldehyde (identified as aromatic dicarbonyls in Fig. 2), and an estimated rate coefficient for 1,2-diacetylbenzene (3.8×10^{-13} cm^3 $molecule^{-1}$ s^{-1}) that is consistent with the reported upper limit value ($< 1.2 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}).

Temperature-dependent data are only available for benzaldehyde. Within the constraints of the approach described above, this was used to provide the optimized temperature dependence expression, $k_{abs(Ph\text{-}C(O)H)} = 5.23 \times 10^{-12} \exp(250/T)$ cm^3 $molecule^{-1}$ s^{-1}.

3.2.3 Nitroarenes and nitrophenols

The set of preferred kinetic data contains rate coefficients for the reactions of OH with a number of nitro-substituted aromatics, namely nitrobenzene, 1-methyl-3-nitrobenzene, 2-nitrophenol and four methyl-substituted 2-nitrophenols. These data were used to optimize the values of $R_{NO2}(\Phi)$ in Table 6, with the values of $R_{OH}(\Phi)$ determined in Sect. 3.2.1 applied where appropriate. During this procedure, it became clear that the value of $k_{abs(Ph\text{-}OH)}$ (also optimized in Sect. 3.2.1) substantially overestimates the importance of H-atom abstraction from the -OH substituent in 2-nitrophenols. The data therefore suggest that an *ortho*- NO_2 group (and possibly also a *para*- NO_2 group) has a strong deactivating effect on this reaction, and the data were best described by reducing its rate by at least an order of magnitude, compared with $k_{abs(Ph\text{-}OH)}$. It was therefore assumed that the rate coefficient previously assigned to -OH groups in aliphatic compounds, $k_{abs(\text{-}OH)} = 1.28 \times 10^{-12} \exp(-660/T)$ cm^3 $molecule^{-1}$ s^{-1}, applies when the aromatic ring is deactivated by the presence of an NO_2 group *ortho*- or *para*- to the -OH substituent. As indicated above, additional information is clearly required to allow a full appraisal of the effects of substituent groups on H-atom abstraction from -OH (or other) substituents in aromatic compounds.

The optimized values of $R_{NO2}(\Phi)$ in Table 6 indicate that NO_2 substituents also strongly deactivate addition of OH to the aromatic ring. As shown in Fig. 2, the resultant values of k_{calc} agree well with k_{obs} for the complete set of nitro-substituted compounds identified above.

4 Reaction of O_2 with OH-aromatic adducts and subsequent chemistry

4.1 OH-aromatic hydrocarbon adducts

A method has been developed to describe the chemistry initiated by reaction of O_2 with the OH-aromatic adducts formed from the addition of OH radicals to aromatic hydrocarbons. Theoretical studies have shown that these reactions, and the subsequent reaction sequences, can be highly complex, involving the participation of geometrical isomers of very different reactivities (e.g. Raoult et al., 2004; Glowacki et al., 2009; Wu et al., 2014; Li et al., 2014; Pan and Wang, 2014; Vereecken, 2018a). The present method does not include the level of detail established in these studies, but aims to provide an empirically-optimized reaction framework incorporating the main features of the mechanisms, as reported in both laboratory and theoretical work.

The reactions of the OH-aromatic hydrocarbon adducts with O_2 are represented to react either by direct α- H atom abstraction, forming HO_2 and a hydroxyarene (phenolic) product, or by β- O_2 addition to the aromatic ring at each of the two carbon atoms adjacent to the -OH substituent to produce β-hydroxy cyclohexadienylperoxy radicals (as illustrated in Fig. 3), such that the overall rate coefficient is given by $k_{\text{abs-O2}} + k_{\text{add-O2(1)}} + k_{\text{add-O2(2)}}$. The H atom abstraction reaction is unavailable for adducts formed from OH addition *ipso*- to an alkyl substitution. There is some evidence for a “dealkylation” pathway from such adducts (e.g. Noda et al., 2009), but this is not currently represented owing to conflicting evidence on its significance (e.g. Aschmann et al., 2010; Loison et al., 2012). In practice, the β- O_2 addition pathways are reversible, such that each value of $k_{\text{add-O2}}$ specifically quantifies the effective irreversible component of the reaction that results in onward removal of the given cyclohexadienylperoxy radical (IUPAC, 2017b; 2017c).

The value of $k_{\text{abs-O2}}$ and the reference value of $k°_{\text{add-O2}}$ for the benzene system (see Table 7) are informed by the calculations of Raoult et al. (2004), but adjusted to give a total rate coefficient of ~2.1×10^{-16} cm^3 $molecule^{-1}$ s^{-1} at 298 K for (the irreversible component of) the reaction of HOC_6H_6 with O_2, as recommended by IUPAC (2017b); and a yield of phenol of ~53 %, which is also consistent with the literature. The value of $k_{\text{abs-O2}}$ is assumed to be independent of the presence of alkyl substituents, but the value of $k_{\text{add-O2}}$ depends on both the degree and distribution of alkyl substituents, and is given by:

$$k_{\text{add-O2}} = k°_{\text{add-O2}} \prod F_i(X), \text{ for } n = 0 \text{ (or 1)} \qquad (6)$$

$$k_{\text{add-O2}} = k°_{\text{add-O2}} \prod F_i(X)/n^{0.5}, \text{ for } n \geq 1 \qquad (7)$$

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. ~~4~~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.

As shown in Fig. 3, the two β-hydroxy cyclohexadienylperoxy radicals formed from O_2 addition are represented to undergo prompt ring closure to produce a common hydroxy-dioxa-bicyclo or “peroxide-bicyclic” radical. This process has been reported to dominate over alternative bimolecular reactions of the peroxy radicals under atmospheric conditions (e.g. Suh et al., 2003; Raoult et al., 2004; Glowacki et al., 2009; Wu et al., 2014; Li et al., 2014; Pan and Wang, 2014). The subsequent chemistry of the peroxide-bicyclic radical is shown in Fig. 4. In each case, the energy-rich radical either promptly isomerizes to form two cyclic epoxy-oxy radicals (as originally proposed by Bartolloti and Edney, 1995), or is stabilized and adds O_2 to form two possible peroxide-bridged peroxy radicals. The cyclic epoxy-oxy radicals undergo ring-opening, followed by reaction with O_2 to generate HO_2 and an epoxydicarbonylene product in each case. Evidence for the formation of ~~such~~ the epoxydicarbonylene products has been reported in experimental studies of a number of atmospheric systems (e.g. Yu and Jeffries, 1997; Kwok et al., 1997; Baltaretu et al., 2009; Birdsall et al., 2010; Birdsall and Elrod, 2011), although it is noted that their formation is calculated to be more important at reduced pressures (e.g. Glowacki et al., 2009; Li et al., 2014). In the present method, prompt isomerization of the peroxide-bicyclic radical to the cyclic epoxy-oxy radicals is assigned a total structure-independent branching ratio of 0.3, divided equally between the two available routes. 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). Inclusion of the “epoxy-oxy” route with this optimized branching ratio ~~in this way~~ results in total prompt HO_2 yields which provide a ~~reasonable~~ 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.

The (stabilized) peroxide-bicyclic radical possesses an allyl resonance, such that addition of O_2 can occur at two possible positions, as shown in Fig. 4. The overall rate coefficient is therefore given by $k_{\text{bc-add(1)}} + k_{\text{bc-add(2)}}$. The reference rate coefficient, $k^{\circ}_{\text{bc-add}}$, for a system with no alkyl substituents at either positions ‘a’ or ‘b’ (see Table 9) was assigned a value of 4×10^{-16} cm^3 molecule^{-1} s^{-1}, based on the total rate coefficient calculated for the peroxide-bicyclic radical formed in the benzene system by Glowacki et al. (2009). Reported calculations for methyl-substituted aromatics (e.g. Wu et al., 2014; Li et al., 2014) suggest that the value of $k_{\text{bc-add}}$ for a given system is also potentially influenced by the presence of alkyl substituents in positions ‘a’ or ‘b’. The addition rate coefficient estimated here is therefore given by:

$$k_{\text{bc-add}} = k^{\circ}_{\text{bc-add}}\, F_a(X)\, F_b(X)$$

(~~6~~8)

Here, $F_a(X)$ and $F_b(X)$ quantify the activating effect of substituents in positions ‘a’ and ‘b’, respectively. The assigned values for an alkyl substituent (given in Table 9) allow a reasonable representation of the relative distribution of α-dicarbonyl products (i.e. glyoxal, methylglyoxal and biacetyl) reported for the series of methyl-substituted aromatics for conditions when the peroxy radicals react predominantly with NO (see Table S2). The large value of F_a(-alkyl) indicates that addition of O_2 at an alkyl-substituted site in the resonant radical is strongly favoured, and can be assumed to be exclusive if only one of the two possible addition sites is alkyl substituted. The more modest influence of a substituent at position ‘b’ (characterized by F_b(-alkyl)) also influences the relative formation of the specific α-dicarbonyls (and their co-products) in cases where neither or both radical sites possess alkyl substituents. It is noted that the treatment of these structurally-complex allyl radicals differs from that reported in the companion paper (Jenkin et al., 2018a) for generic allyl radicals, and is specific to this type of structure.

The calculated yields presented in Table S2 also take account of minor formation of nitrate products from the peroxy + NO reactions (see Fig. 4), for which the currently estimated branching ratios vary from zero to 0.11 depending on peroxy radical structure. This is described in more detail elsewhere (Jenkin et al., 2018b). Table S2 also compares the calculated “prompt” yields of HO_2 with those reported by Nehr et al. (2011; 2012) and the total nitrate yields with those reported by Rickard et al. (2010) and Elrod (2011). Fig. 5 presents a correlation plot of calculated and observed yields of hydroxyarenes (total and specific), α-dicarbonyls (total and specific), nitrates (total) and prompt HO_2, which confirms that the methods presented above provide a reasonable representation of the first-generation OH-initiated chemistry of aromatic hydrocarbons. 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.

4.2 OH-aromatic oxygenate adducts

Product and mechanistic information on the reactions of adducts formed from the addition of OH radicals to aromatic oxygenates appears to be limited to those formed from hydroxyarene (phenolic) compounds (e.g. Olariu et al., 2002; Berndt et al., 2003; Coeur-Tourneur et al., 2006). Those studies have established that 1,2-dihydroxyarenes (catechols) and 1,4-benzoquinones are formed as ring-retaining products of the OH-initiated oxidation of phenol and cresols. On the basis of the reported information, the pathways presented in Fig. 6 are applied in relation to hydroxy-substituted aromatic compounds. Addition of OH at an unsubstituted carbon *ortho*- to an existing hydroxy substituent is assumed to result in exclusive formation of HO_2 and a 1,2-dihydroxy product, following subsequent reaction of the adduct with O_2. Addition of OH *para*- to an existing hydroxy substituent is assumed to result in formation of HO_2 and a reactive 4-hydroxy-cyclohexa-2,5-dienone product, following subsequent reaction of the adduct with O_2. In cases where the initial addition of OH occurs at an unsubstituted carbon in the aromatic compound, further reaction of OH with the 4-hydroxy-cyclohexa-2,5-dienone partially produces a 1,4-benzoquinone product (as shown in Fig. 6), based on the methods applied to aliphatic compounds (Jenkin et al., 2018a).

For other OH-aromatic oxygenate adducts, the mechanisms applied to OH-aromatic hydrocarbon adducts (see Sect. 4.1) are provisionally applied, in the absence of information. Within the framework described in Sect. 4.1, some additional assumptions are applied in relation to addition of O_2 to the (stabilized) resonant peroxide bicyclic radical, these being consistent with those applied generally to allyl radicals containing oxygenated substituents (Jenkin et al., 2018a). If the resonant peroxide bicyclic radical contains an oxygenated substituent at either or both positions ‘a’, addition of O_2 is assumed to occur exclusively at the site possessing the substituent that is higher in the following list: -OH/-OR/-OOH/-OOR > -OC(=O)H/-OC(=O)R > alkyl/-H > -C(=O)H/-C(=O)R > -C(=O)OH/-C(=O)OR > $-ONO_2$ > $-NO_2$ (substituents with more remote oxygenated groups are treated as alkyl groups). If both sites possess a substituent of the same rating, O_2 addition is assumed to occur equally at each site. An oxygenated substituent at position ‘b’ is assumed to have no effect (Table 9).

5 Reactions of organic radicals formed from OH attack on substituent groups

Carbon-centred organic radicals (R) formed from H-atom abstraction from, or OH addition to, substituent groups in aromatic compounds generally react as described for those formed from aliphatic organic compounds in the companion paper (Jenkin et al., 2018a). In the majority of cases, therefore, they react rapidly and exclusively with molecular oxygen (O_2) under tropospheric conditions, to form the corresponding thermalized peroxy radicals (RO_2), the chemistry of which will be summarized elsewhere (Jenkin et al., 2018b):

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

(M denotes a third body, most commonly, N_2). Abstraction of hydrogen from hydroxy and hydroperoxy substituents groups in aromatic VOCs results in formation of phenoxy and phenyl peroxy radicals, respectively. The representation of phenyl peroxy radical chemistry will be considered elsewhere, along with that of other peroxy radicals (Jenkin et al., 2018b). The chemistry of phenoxy radicals differs from that of oxy radicals in general, in that they apparently do not react with O_2, isomerize or decompose under tropospheric conditions. Kinetics studies for the phenoxy radical itself (C_6H_5O) indicate that reactions with NO, NO_2 and O_3 are likely to be competitive under ambient conditions (Platz et al., 1998; Berho et al., 1998; Tao and Li, 1999), with evidence also reported for reaction with HO_2 at room temperature (Jenkin et al., 2007; 2010) and in low temperature combustion systems (Herbinet et al., 2013). As summarized in Table 10, the reactions with NO_2, O_3 and HO_2 are generally represented for a given phenoxy radical, although reaction with NO_2 is unavailable for phenoxy radicals with two *ortho*- substituents, because formation of a 1-hydroxy-2-nitroarene product is precluded. The reaction with NO is not represented because the reverse reaction is reported to occur on the timescale of about one minute (Berho et al., 1998).

6 Conclusions

A structure activity relationship (SAR) method has been developed to estimate rate coefficients for the reactions of the OH radical with aromatic organic species. This group contribution method was optimized using a database including a set preferred rate coefficients for 67 species. The overall performance of the SAR in determining log k_{298K} is now summarized. The distribution of errors (log k_{calc}/k_{obs}), the Root Mean Squared Error (RMSE), the Mean Absolute Error (MAE) and the Mean Bias Error (MBE) were examined to assess the overall reliability of the SAR. The RMSE, MAE and MBE are here defined as:

$$RMSE = \sqrt{\frac{1}{n}\sum_{i=1}^{n}(\log k_{calc} - \log k_{obs})^2}$$

(~~7~~9)

$$MAE = \frac{1}{n}\sum_{i=1}^{n}|\log k_{calc} - \log k_{obs}|$$

(~~8~~10)

$$MBE = \frac{1}{n}\sum_{i=1}^{n}(\log k_{calc} - \log k_{obs})$$

(~~9~~11)

where *n* is the number of species in the dataset. The assessment was performed to identify possible biases within a series of categories, namely hydrocarbons, monofunctional oxygenated species and bifunctional oxygenated species. Errors computed for these subsets are summarized Fig. 7, where they are compared with those for the corresponding categories of aliphatic organic compound, as reported in the companion paper (Jenkin et al., 2018a).

The calculated log k_{298K} shows no significant bias, with MBE remaining below 0.02 log units for the various subsets, and with median values of the error distributions close to zero. The reliability of the SAR decreases with the number of oxygenated functional groups on the aromatic ring, with the RMSE increasing from 0.06 for hydrocarbons to 0.07 for monofunctional and 0.08 for bifunctional species, i.e. a relative error for the calculated k_{298K} of a 15 %, 17 % and 20 %, respectively. 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. Finally, for the full database, the SAR gives generally reliable k_{298K} estimates, with a MAE of 0.04 and a RMSE of 0.07, corresponding to an overall agreement of the calculated k_{298K} within 17%.

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References

Alarcón, Strekowski, R. and Zetzsch, C.: Reversible addition of the OH radical to *p*-cymene in the gas phase: kinetic analysis assuming formation of a single adduct. Part 1, Phys. Chem. Chem. Phys., 15, 20105-20114, 2013.

Alarcón, Bohn, B. and Zetzsch, C., Rayez, M.-T. and Rayez, J.-C.: Reversible addition of the OH radical to *p*-cymene in the gas phase: multiple adduct formation. Part 2, Phys. Chem. Chem. Phys., 16, 17315-17326, 2014.

Alarcón, Bohn, B. and Zetzsch, C.: Kinetic and mechanistic study of the reaction of OH radicals with methylated benzenes: 1,4-dimethyl-, 1,3,5-trimethyl-, 1,2,4,5-, 1,2,3,5- and 1,2,3,4-tetramethyl-, pentamethyl-, and hexamethylbenzene, Phys. Chem. Chem. Phys., 17, 13053-13065, 2015.

Anderson, R. S., Iannone, R., Thompson, A. E. and Rudolph, J.: Carbon kinetic isotope effects in the gas-phase reactions of aromatic hydrocarbons with the OH radical at 296 ± 4 K, Geophys. Res. Lett., 31, L15108, doi:10.1029/2004GL020089, 2004

Andreae, M. O. and Crutzen, P. J.: Atmospheric aerosols: biogeochemical sources and role in atmospheric chemistry, Science, 276, 1052–1058, 1997.

Aschmann, S. M., Arey, J. and Atkinson, R.: Extent of H-atom abstraction from OH + *p*-cymene and upper limits to the formation of cresols from OH + *m*-xylene and OH + *p*-cymene. Atmos. Environ., 44, 3970-3975, 2010.

Aschmann, S. M., Arey, J. and Atkinson, R.: Formation of p-cymene from OH + γ-terpinene: H-atom abstraction from the cyclohexadiene ring structure, Atmos. Environ., 45, 4408−4411, 2011.

Aschmann, S. M., Arey, J. and Atkinson, R.: Rate constants for the reactions of OH radicals with 1,2,4,5-tetramethylbenzene, pentamethylbenzene, 2,4,5-trimethylbenzaldehyde, 2,4,5-trimethylphenol, and 3-methyl-3-hexene-2,5-dione and products of OH + 1,2,4,5-tetramethylbenzene. J. Phys. Chem. A, 117, 2556−2568, 2013.

Atkinson, R.: Kinetics and mechanisms of the gas-phase reactions of the hydroxyl radical with organic compounds. J. Phys. Chem. Ref. Data, Monograph 1, 1989.

Atkinson, R., Aschmann, S. M. and Arey, J.: Reactions of OH and NO_3 radicals with phenol, cresols, and 2-nitrophenol at 296 ± 2 K, Environ. Sci. Technol., 26, 1397-1403, 1992.

Atkinson, R. and Aschmann, S. M.: Products of the gas-phase reactions of aromatic hydrocarbons: Effect of NO_2 concentration, Int. J. Chem. Kinet. 26, 929–944, 1994.

Atkinson, R. and Arey, J.: Atmospheric degradation of volatile organic compounds, Chem. Rev., 103, 4605-4638, 2003.

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

Baltaretu, C. O., Lichtman, E. I., Hadler, A. B. and Elrod, M. J.: Primary atmospheric oxidation mechanism for toluene, J. Phys. Chem. A, 113, 221−230, 2009.

Bartolotti, L. J. and Edney, E. O.: Density functional theory derived intermediates from the OH initiated atmospheric oxidation of toluene, Chem. Phys. Lett., 245, 119−122, 1995.

Bedjanian, Y., Morin, J. and Romanias, M. N.: Gas-phase reaction of hydroxyl radical with *p*-cymene over an extended temperature range, J. Phys. Chem. A, 119, 11076−11083, doi: 10.1021/ acs.jpca.5b08478, 2015.

Bejan, I., Barnes, I., Olariu, R., Zhou, S., Wiesen, P. and Benter, T: Investigations on the gas-phase photolysis and OH radical kinetics of methyl-2-nitrophenols, Phys. Chem. Chem. Phys., 9, 5686–5692, 2007.

Bejan, I., Schürmann, A., Barnes, I. and Benter, T. : Kinetics of the gas-phase reactions of OH radicals with a series of trimethylphenols, Int. J. Chem. Kinet., 44, 117-124, 2012.

Berho, F. and Lesclaux, R.: (1997)

Berho, F., Caralp, F., Rayez, M. T., Lesclaux, R., and Ratajczak, E.: Kinetics and thermochemistry of the reversible combination reaction of the phenoxy radical with NO, J. Phys. Chem. A, 102, 1-8, 1998.

Bernard, F., Magneron, I., Eyglunent, G., Daële, V. and Wallington, T. J.: Atmospheric chemistry of benzyl alcohol: kinetics and mechanism of reaction with OH radicals, Environ. Sci. Technol., 47, 3182-3189, 2013.

Berndt, T. and Böge, O.: Gas-phase reaction of OH radicals with phenol, Phys. Chem. Chem. Phys., 5, 342-350, 2003.

Berndt, T. and Böge, O.: Formation of phenol and carbonyls from the atmospheric reaction of OH radicals with benzene, Phys. Chem. Chem. Phys., 8, 1205-1214, 2006.

Berndt, T., Böge, O., Kind, I. and Rolle, W.: Reaction of NO_3 radicals with 1,3-cyclohexadiene, α-terpinene, and α-phellandrene: kinetics and products. Ber. Bunsenges. Phys. Chem., 100, 462-469, 1996.

Bignozzi, C., Maldotti, A., Chiorboli, C., Bartocci, C. and Carassiti, V.: Kinetics and mechanism of reactions between aromatic olefins and hydroxyl radicals, Int. J. Chem. Kinet., 13, 1235-1242, 1981.

Birdsall, A. W. and Elrod, M. J.: Comprehensive NO-dependent study of the products of the oxidation of atmospherically relevant aromatic compounds, J. Phys. Chem. A, 115, 5397–5407, 2011.

Birdsall, A. W., Andreoni, J. F. and Elrod, M. J.: Investigation of the role of bicyclic peroxy radicals in the oxidation mechanism of toluene, J. Phys. Chem. A, 114, 10655–10663, 2010.

Bloss, C., Wagner, V., Jenkin, M. E., Volkamer, R., Bloss, W. J., Lee, J. D., Heard, D. E., Wirtz, K., Martin-Reviejo, M., Rea, G., Wenger, J. C. and Pilling, M. J.: Development of a detailed chemical mechanism (MCM v3.1) for the atmospheric oxidation of aromatic hydrocarbons. Atmos. Chem. Phys., 5, 641-644, 2005.

Bohn, B. and Zetzsch, C.: Kinetics and mechanism of the reaction of OH with the trimethylbenzenes – experimental evidence for the formation of adduct isomers, Phys. Chem. Chem. Phys., 14, 13933–13948, 2012.

Bouvier-Brown, N. C., Goldstein, A. H., Gilman, J. B., Kuster, W. C., and de Gouw, J. A.: In-situ ambient quantification of monoterpenes, sesquiterpenes, and related oxygenated compounds during BEARPEX 2007: implications for gas- and particle-phase chemistry, Atmos. Chem. Phys., 9, 5505-5518, https://doi.org/10.5194/acp-9-5505-2009, 2009.

Calvert, J. G., Atkinson, R., Becker, K.H., Kamens, R. M., Seinfeld, J. H., Wallington, T. J. and Yarwood, G.: Mechanisms of atmospheric oxidation of the aromatic hydrocarbons, Oxford University Press, Oxford. ISBN 0-19514628-X, 2002.

Cho, J., Roueintan, M. and Li, Z.: Kinetic and dynamic investigations of OH reaction with styrene, J. Phys. Chem. A, 118, 9460-9470, 2014.

Clifford, G., Rea, G., Thuener, L. P. and Wenger, J: Atmospheric impact of xylene oxidation products. Presented at IGAC Conference, *Atmospheric Chemistry in the Earth System: from Regional Pollution to Global Change*, Crete, Greece, 18-25 September 2002. Available at: https://www.ucc.ie/en/media/research/crac/grainne_poster_crete_2002.pdf

Colomb, A., Jacob, V., Kaluzny, P. and Baussand, P.: Gas-phase reactions between the OH-radical and *o*-, *m*-, *p*-ethyltoluene and *n*-nonane in air. Int. J. Chem. Kinet., 36, 367–378, 2004.

Coeur-Tourneur, C., Henry, F., Janquin, M. -A. and Brutier, L.: Gas-phase reaction of hydroxyl radicals with *m*-, *o*- and *p*-cresol, Int. J. Chem. Kinet., 38, 553-562, 2006.

Derwent, R. G., Jenkin, M. E. and Saunders, S. M.: Photochemical ozone creation potentials for a large number of reactive hydrocarbons under European conditions, Atmos. Environ. 30, 181-199, 1996.

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

Fan, J. and Zhang, R.: Atmospheric oxidation mechanism of *p*-xylene: a Density Functional Theory study. J. Phys. Chem. A, 110, 7728-7737, 2006.

Fan, J. and Zhang, R.: Density Functional Theory study on OH-initiated atmospheric oxidation of *m*-xylene. J. Phys. Chem. A, 112, 4314-4323, 2008.

Gentner, D. R., Jathar, S. H., Gordon, T. D., Bahreini R., Day, D. A., El Haddad, I., Hayes, P. L., Pieber, S. M., Platt, S. M., de Gouw, J., Goldstein, A. H., Harley, R. A., Jimenez, J. L., Prévôt, A. S. H., Robinson, A. L.: Review of urban secondary organic aerosol formation from gasoline and diesel motor vehicle emissions, Environ. Sci. Technol., 51 (3), 1074-1093, 2017.

Glowacki, D. R., Wang, L., and Pilling, M. J.: Evidence of formation of bicyclic species in the early stages of atmospheric benzene oxidation, J. Phys. Chem. A, 113, 5385−5396, 2009.

Haagen-Smit, A. J., Fox, M. M.: Photochemical ozone formation with hydrocarbons and automobile exhaust., J. Air Pollut. Control Assoc., 4, 105–109 1954.

Hallquist, M., Wenger, J. C., Baltensperger, U., Rudich, Y., Simpson, D., Claeys, M., Dommen, J., Donahue, N. M., George, C., Goldstein, A. H., Hamilton, J. F., Herrmann, H., Hoffmann, T., Iinuma, Y., Jang, M., Jenkin, M. E, Jimenez, J. L., Kiendler-Scharr, A., Maenhaut, W., McFiggans, G., Mentel, Th. F., Monod, A., Prévôt, A. S. H., Seinfeld, J. H., Surratt, J. D., Szmigielski, R., Wildt, J.: The formation, properties and impact of secondary organic aerosol: current and emerging issues, Atmos. Chem. Phys., 9, 5155−5236, 2009.

Harrison, J. C. and Wells, J. R.: Gas-phase chemistry of benzyl alcohol: reaction rate constants and products with OH radical and ozone, Atmos. Environ., 43, 798-804, 2009.

Hays, M. D., Geron, C. D., Linna, K. J., Smith, N. D. and Schauer, J. J.: Speciation of gas-phase and fine particle emissions from burning of foliar fuels, Environ. Sci. Technol., 36, 2281-2295, 2002.

Helmig D. et al.:Vertical profiling and determination of landscape fluxes of biogenic nonmethane hydrocarbons within the planetary boundary layer in the Peruvian Amazon. J. Geophys. Res. Atmos., 103 (D19), 25519-25532, 1998.

Herbinet, O., Husson, B., Ferrari, M., Glaude, P.A. and Battin-Leclerc, F.: Low temperature oxidation of benzene and toluene in mixture with *n*-decane, Proc. Combust. Inst., 34(1), 297–305, 2013.

Huang M., Wang, Z., Hao, L. and Zhang, W.: Density functional theory study on the mechanism of OH-initiated atmospheric photooxidation of ethylbenzene. J. Molec. Struct.: THEOCHEM, 944, 21–33, 2010.

Huang M., Wang, Z., Hao, L. and Zhang, W.: Theoretical investigation on the mechanism and kinetics of OH radical with *m*-xylene, Comput. Theor. Chem., 965, 285–290, 2011.

Iuga, C., Galano, A. and Vivier-Bunge, A.: Theoretical investigation of the OH-initiated oxidation of benzaldehyde in the troposphere, ChemPhysChem, 9, 1453-1459, 2008.

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation.: http://iupac.pole-ether.fr/htdocs/datasheets/pdf/HOx_AROM2_HO_toluene.pdf, 2017a.

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation.: http://iupac.pole-ether.fr/htdocs/datasheets/pdf/AROM_RAD1_HOC6H6_O2.pdf, 2017b.

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation.: http://iupac.pole-ether.fr/htdocs/datasheets/pdf/AROM_RAD4_HOC7H8_O2.pdf, 2017c.

Jenkin, M. E. and Clemitshaw, K. C.: Ozone and other secondary photochemical pollutants: chemical processes governing their formation in the planetary boundary layer, Atmos. Environ., 34, 2499–2527, 2000.

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

Jenkin, M. E., Hurley, M. D., and Wallington, T. J.: Investigation of the radical product channel of the $CH_3C(O)O_2 + HO_2$ reaction in the gas phase, Phys. Chem. Chem. Phys., 9, 3149-3162, 2007.

Jenkin, M. E., Hurley, M. D., and Wallington, T. J.: Investigation of the radical product channel of the $CH_3OCH_2O_2 + HO_2$ reaction in the gas phase, J. Phys. Chem. A, 114, 408-416, 2010.

Jenkin, M. E., Derwent, R. G., and Wallington, T. J.: Photochemical ozone creation potentials for volatile organic compounds: Rationalization and estimation, Atmos. Environ., 163, 128-137, 2017.

Jenkin, M. E., Valorso, R., Aumont, B., Rickard, A. R. and Wallington, T. J.: Estimation of rate coefficients and branching ratios for reactions of OH with aliphatic organic compounds for use in automated mechanism construction, Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2018-145, in review~~in preparation~~, 2018a.

Jenkin et al.: Estimation of rate coefficients and branching ratios for reactions of organic peroxy radicals for use in automated mechanism construction, in preparation, 2018b.

Klotz, B., Sørensen, S., Barnes, I., Becker, K.H., Etzkorn, T., Volkamer, R., Platt, U., Wirtz, K. and Martín-Reviejo, M.: Atmospheric oxidation of toluene in a large volume outdoor photoreactor: in situ determination of ring-retaining product yields, J. Phys. Chem. A, 102, 10289-10299, 1998.

Kwok, E.S.C. and Atkinson R.: Estimation of hydroxyl radical reaction rate constants for gas-phase organic compounds using a structure-reactivity relationship: an update, Atmos. Environ., 29, 1685−1695, 1995.

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 NO_x, J. Chem. Soc., Faraday Trans., 93(16), 2847-2854, 1997.

Lewis, A. C., Evans, M. J., Hopkins, J. R., Punjabi, S., Read, K. A., Purvis, R. M., Andrews, S. J., Moller, S. J., Carpenter, L. J., Lee, J. D., Rickard, A. R., Palmer, P. I., and Parrington, M.: The influence of biomass burning on the global distribution of selected non-methane organic compounds, Atmos. Chem. Phys., 13, 851-867, https://doi.org/10.5194/acp-13-851-2013, 2013.

Li, Y. and Wang, Y.: The atmospheric oxidation mechanism of 1,2,4-trimethylbenzene initiated by OH radicals, Phys. Chem. Chem. Phys., 16, 17908-17917, 2014.

Loison, J-C., Rayez, M-T., Rayez, J-T., Gratien, A., Morajkar, P., Fittschen, P. and Villenave, E.: Gas-phase reaction of hydroxyl radical with hexamethylbenzene. J. Phys. Chem. A, 116, 12189−12197, 2012.

Maleknia, S. D., Bell, T. L. and Adams, M. A.: PTR-MS analysis of reference and plant-emitted volatile organic compounds, Int. J. Mass. Spectrom., 262, 203-210, 2007.

Mehta, D., Nguyen, A., Montenegro, A. and Li, Z.: A kinetic study of the reaction of OH with xylenes using the relative rate/discharge flow/mass spectrometry technique, J. Phys. Chem. A, 113, 12942–12951, 2009.

Misztal, P. K., Owen, S. M., Guenther, A. B., Rasmussen, R., Geron, C., Harley, P., Phillips, G. J., Ryan, A., Edwards, D. P., Hewitt, C. N., Nemitz, E., Siong, J., Heal, M. R., and Cape, J. N.: Large estragole fluxes from oil palms in Borneo, Atmos. Chem. Phys., 10, 4343-4358, https://doi.org/10.5194/acp-10-4343-2010, 2010.

Misztal , P. K., Hewitt, C. N., Wildt, J., Blande, J. D., Eller, A. S. D., Fares, S., Gentner, D. R., Gilman, J. B., Graus, M., Greenberg, J., Guenther, A. B., Hansel, A., Harley, P., Huang, M., Jardine, K., Karl, T., Kaser, L., Keutsch, F. N., Kiendler-Scharr, A., Kleist, E., Lerner, B. M., Li, T., Mak, J., Nölscher, A. C.. Schnitzhofer, R., Sinha, V., Thornton, B., Warneke, C., Wegener, F., Werner, C., Williams, J., Worton, D. R., Yassaa, N. and Goldstein, A. H.: Atmospheric benzenoid emissions from plants rival those from fossil fuels, Scientific Reports, 5, Article number 12064, doi:10.1038/srep12064, 2015.

Mousavipour, S. H. and Homayoon, Z.:Multichannel RRKM-TST and CVT rate constant calculations for reactions of CH_2OH or CH_3O with HO_2, J. Phys. Chem. A, 115, 3291-3300, 2011.

Nehr, S, Bohn, B., Fuchs, H., Hofzumahaus, A. and Wahner, A: HO_2 formation from the OH + benzene reaction in the presence of O_2, Phys. Chem. Chem. Phys., 13, 10699–10708, 2011.

Nehr, S, Bohn, B. and Wahner, A: Prompt HO_2 formation following the reaction of OH with aromatic compounds under atmospheric conditions, J. Phys. Chem. A, 116, 6015-6026, 2012.

Nishino, N., Arey, J. and Atkinson, R: Formation yields of glyoxal and methylglyoxal from the gas-phase OH radical-initiated reactions of toluene, xylenes, and trimethylbenzenes as a function of NO_2 concentration, J. Phys. Chem. A, 114, 10140−10147, 2010.

Noda, J., Volkamer, R., and Molina, M.J.: Dealkylation of alkylbenzenes: a significant pathway in the toluene, o-, m-, and p-xylene + OH reaction, J. Phys. Chem. A., 113, 9658-9666, 2009.

Odum, J. R., Jungkamp, T. P. W., Griffin, R. J., Forstner, H. J. L., Flagan, R. C. and Seinfeld, J. H.: Aromatics, reformulated gasoline, and atmospheric organic aerosol formation. Environ. Sci. Technol., 31 (7), 1890-1897, 1997.

Olariu, R. I., Klotz, B., Barnes, I., Becker, K. H., and Mocanu, R.: FT-IR study of the ring-retaining products from the reaction of OH radicals with phenol, o-, m-, and p-cresol, Atmos. Environ., 36 (22), 3685-3697, 2002.

Owen, S. M., Boissard, C., and Hewitt, C. N.: Volatile organic compounds (VOCs) emitted from 40 Mediterranean plant species: VOC speciation and extrapolation to habitat scale, Atmos. Environ., 35, 5393-5409, 2001.

Pan, S. and Wang, L.: Atmospheric oxidation mechanism of m-xylene initiated by OH radical, J. Phys. Chem. A, 118, 10778-10787, 2014.

Passant, N. R.: Speciation of UK emissions of non-methane volatile organic compounds. AEA Technology Report ENV-0545. Culham, Abingdon, United Kingdom, 2002.

Peeters, J., Vandenberk, S., Piessens, E. and Pultau, V.: H-atom abstraction in reactions of cyclic polyalkenes with OH, Chemosphere, 38, 1189-1195, 1999.

Peeters, J., Boullart, W., Pultau, V., Vandenberk, S. and Vereecken, L.: Structure-activity relationship for the addition of OH to (poly)alkenes: site-specific and total rate constants, J. Phys. Chem. A, 111, 1618-1631, 2007.

Perry, R. A., Atkinson, R. and Pitts, J. N.: Kinetics and mechanism of the gas phase reaction of OH radicals with methoxybenzene and o-cresol over the temperature range 299- 435 K, J. Phys. Chem., 81, 1607-1611, 1977.

Platz, J., Nielsen, O. J., Wallington, T. J., Ball, J. C., Hurley, M. D., Straccia, A. M., Schneider, W. F., and Sehested, J.: Atmospheric chemistry of the phenoxy radical, J. Phys. Chem. A, 102, 7964-7974, 1998.

Raoult, S, Rayez, M-. T. , Rayez, J-. C. and Lesclaux, R.: Gas phase oxidation of benzene: Kinetics, thermochemistry and mechanism of initial steps, Phys. Chem. Chem. Phys., 6, 2245-2253, 2004.

Rickard, A. R., Wyche, K. P., Metzger, A., Monks, P. S., Ellis, A. M., Dommen, J., Baltensperger, U., Jenkin, M. E. and Pilling M. J.: Gas phase precursors to anthropogenic secondary organic aerosol: using the Master Chemical Mechanism to probe detailed observations of 1,3,5-trimethylbenzene photo-oxidation, Atmos. Environ., 44, 5423-5433, 2010.

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

Smith, D. F., McIver, C. D., and Kleindienst, T. E.: Primary product distribution from the reaction of hydroxyl radicals with toluene at ppb NO_x mixing ratios, J. Atmos. Chem. 30, 209–228, 1998.

Smith, D. F., Kleindienst, T. E., and McIver, C. D.: Primary product distributions from the reaction of OH with m-, p-xylene, 1,2,4- and 1,3,5-trimethyl benzene, J. Atmos. Chem., 34, 339-364, 1999.

Suh, I., Zhang, D., Zhang, R., Molina, L. T. and Molina, M. J.: Theoretical study of OH addition reaction to toluene. Chem. Phys. Lett., 364, 454–462, 2002.

Suh, I., Zhang, R., Molina, L. T. and Molina, M. J.: Oxidation mechanism of aromatic peroxy and bicyclic radicals from OH-toluene reactions, J. Am. Chem. Soc., 125, 12655−12665, 2003.

Tao, Z. and Li, Z.: A kinetics study on reactions of C_6H_5O with C_6H_5O and O_3 at 298K, Int. J. Chem. Kinetics, 31, 65-72, 1999.

Tuazon, E., Arey, J., Atkinson, R. and Aschmann, S.: Gas-phase reactions of vinylpyridine and styrene with OH and NO_3 radicals and O_3, Environ. Sci. Technol., 27, 1832-1841, 1993.

Ulman M. et al.: Determination of volatile organic compounds (VOCs) in the atmosphere over central Siberian forest and southern part of European Taiga in Russia, Chemia Analityczna, 52, 435-451, 2007.

Vereecken, L.: Reaction mechanisms for the atmospheric oxidation of monocyclic aromatic compounds, in Advances in Atmospheric Chemistry, Vol. 2, Barker, J. R., Allison, S., Wallington, T. J. (Ed.), Accepted for publication, 2018a.

Vereecken, L.: Interactive comment on “Estimation of rate coefficients and branching ratios for gas-phase reactions of OH with aromatic organic compounds for use in automated mechanism construction” by Michael E. Jenkin et al., Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2018-146-SC1, 2018b.

Volkamer, R., Platt, U., and Wirtz, K.: Primary and secondary glyoxal formation from aromatics: experimental evidence for the bicycloalkyl-radical pathway from benzene, toluene and p-xylene, J. Phys. Chem. A, 105, 7865–7874, 2001.

Volkamer, R., Klotz, B., Barnes, I., Imamura, T., Wirtz, K., Washida, N., Becker, K. H., and Platt, U.: OH-initiated oxidation of benzene – Part I. Phenol formation under atmospheric conditions, Phys. Chem. Chem. Phys., 4 (9), 1598–1610, 2002.

Went, F. W.: Blue hazes in the atmosphere, Nature, 187, 641–645, 1960.

Wu, R., Pan, S., Li, Y. and Wang., L.: Atmospheric oxidation mechanism of toluene. J. Phys. Chem. A, 118, 4533−4547, 2014.

Yu, J. Z. and Jeffries, H. E.: Atmospheric photooxidation of alkylbenzenes 2. Evidence for formation of epoxide intermediates, Atmos. Environ., 31 (15), 2281–2287, 1997.

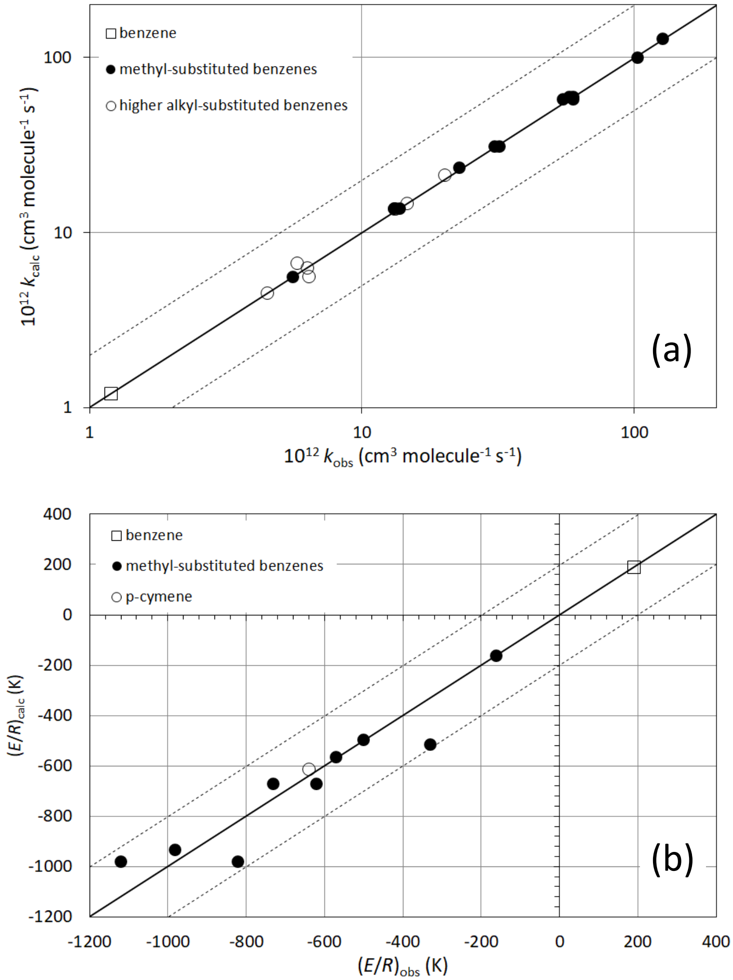


Figure 1: (a) A log-log correlation of k_{calc} and k_{obs} at 298 K for benzene, methyl-substituted benzenes and higher alkyl-substituted benzenes. The broken lines show the ~~± a~~ factor of 2 range; (b) A correlation of the temperature coefficients $(E/R)_{calc}$ and $(E/R)_{obs}$ for the same compound classes. The broken lines show the ± 200 K range.

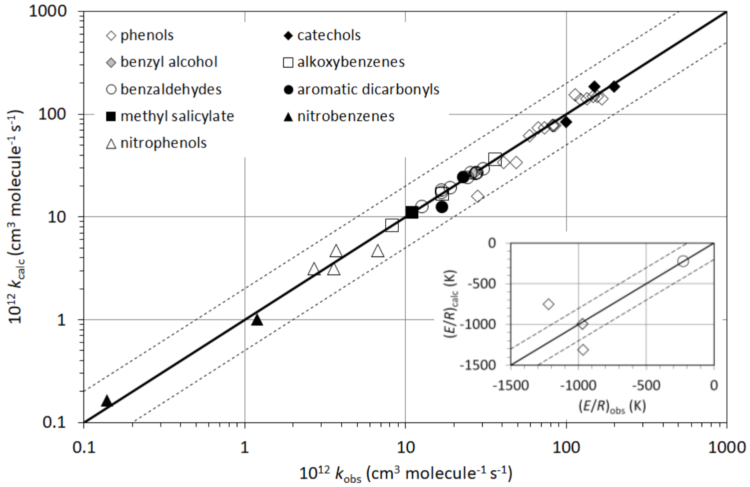


Figure 2: A log-log correlation of k_{calc} and k_{obs} at 298 K for oxygenated aromatic compounds. The broken lines show the ~~± a~~ factor of 2 range. The inset plot shows a correlation of the temperature coefficients $(E/R)_{calc}$ and $(E/R)_{obs}$ for phenol, cresols and benzaldehyde (note that the data points for *o*- and *p*-cresol are coincident at -970 K, -996 K). The broken lines show the ± 200 K range.

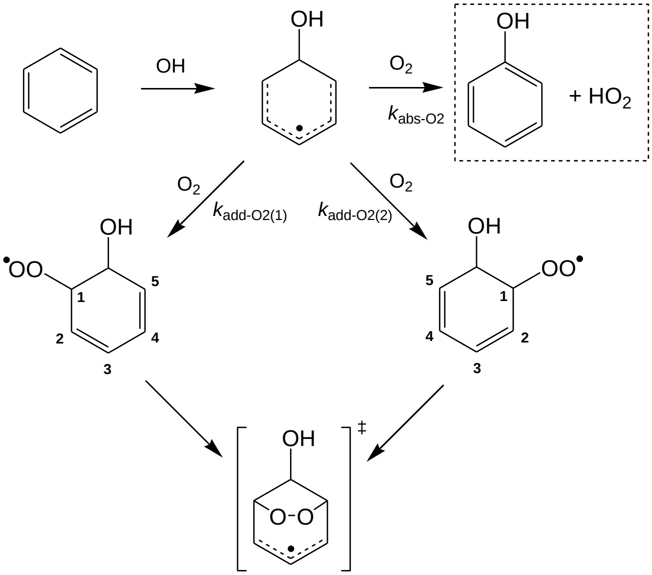


Figure 3: Schematic representation of the reaction of OH-aromatic adducts with O_2, with alkyl substituents omitted for clarity. The abstraction pathway (for which the rate coefficient is $k_{abs\text{-}O2}$) requires the presence of an α- H atom, and is therefore unavailable for adducts formed from OH addition *ipso*- to an alkyl group. The rate coefficients for the two addition pathways ($k_{add\text{-}O2(1)}$ and $k_{add\text{-}O2(2)}$) depend on the number and distribution of alkyl substituents at positions 1 to 5 (see Sect 4.1 and Table 8). The resultant β-hydroxy cyclohexadienylperoxy radicals are assumed to undergo prompt ring closure to produce a common "peroxide-bicyclic" radical.

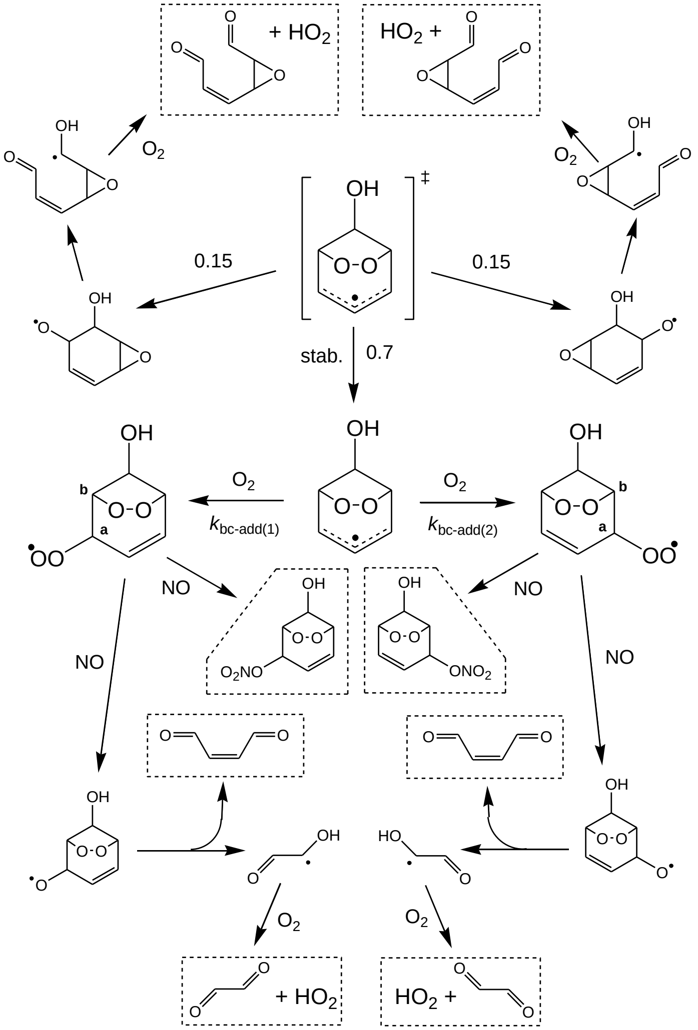


Figure 4: Schematic representation of the mechanism following formation of the "peroxide-bicyclic" radical, as shown in Fig. 3, with alkyl substituents omitted for clarity. The initial energy-rich "peroxide-bicyclic" radical is assumed to isomerize as shown with a total probability of 30 % in competition with stabilization. Addition of O$_2$ to the stabilized radical can occur at two positions. The rate coefficients for the two addition pathways ($k_{\text{bc-add(1)}}$ and $k_{\text{bc-add(2)}}$) depend on the number and distribution of alkyl substituents at positions 'a' and 'b' in each case (see Sect. 4.1 and Table 9). The resultant peroxy radicals undergo conventional bimolecular reactions, with only those involving NO shown here. The oxy radicals formed from propagating channels decompose to form α-dicarbonyls and (at least partially) unsaturated 1,4-dicarbonyl products, in conjunction with HO$_2$, via the generally accepted mechanism shown.

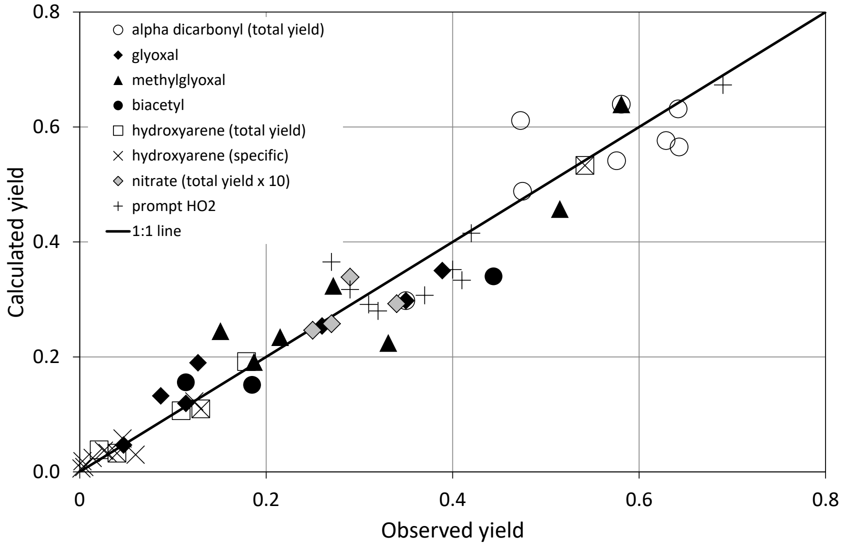


Figure 5: Correlation of calculated and observed yields of hydroxyarenes (total and specific), α-dicarbonyls (total and specific), peroxide-bicyclic nitrates (total) and prompt HO_2, formed from the degradation of benzene and methyl-substituted aromatic hydrocarbons. Observed data taken from Atkinson and Aschmann (1994), Smith et al. (1998; 1999), Klotz et al. (1998), Volkamer et al. (2001; 2002), Berndt and Böge (2006), Noda et al. (2009), Rickard et al. (2010), Elrod (2011) and Nehr et al. (2011; 2012), as summarized in Tables S1 and S2.

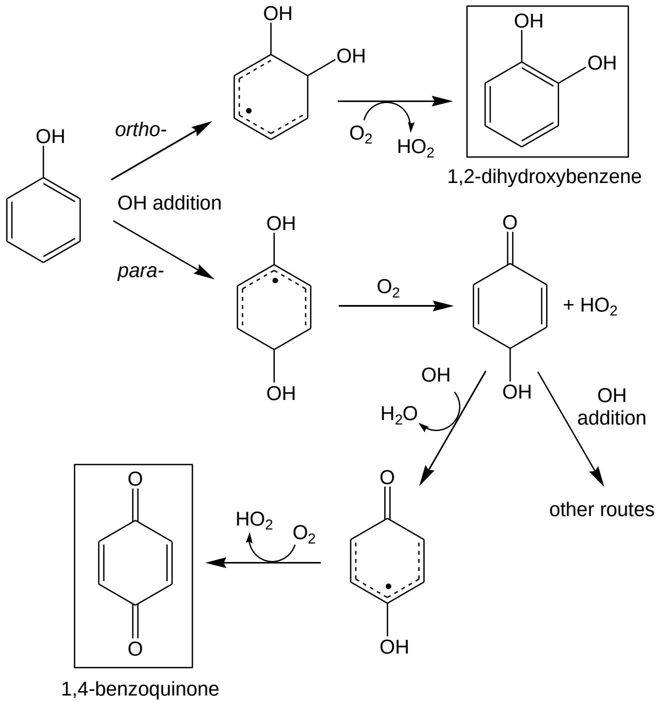
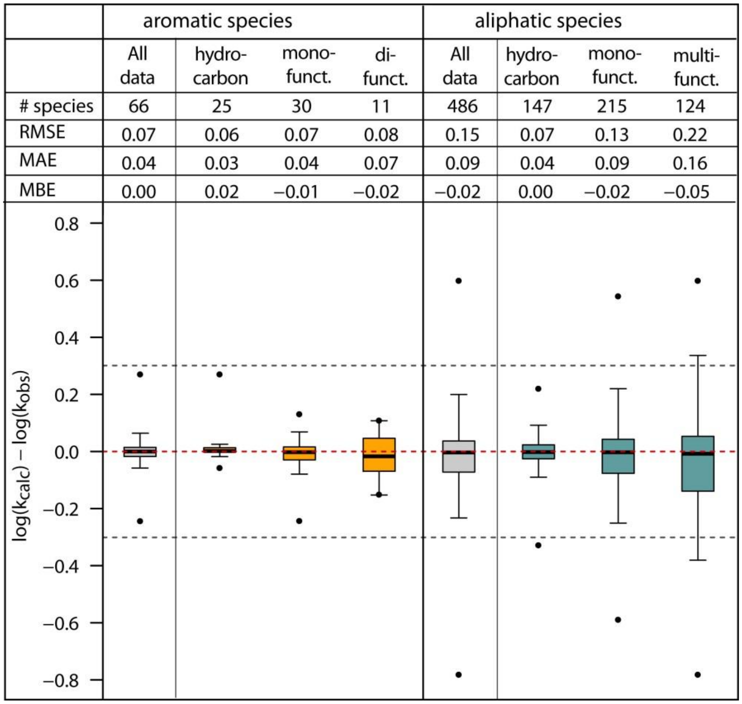


Figure 6: Routes applied following OH addition at an unsubstituted carbon *ortho-* or *para-* to an existing OH substituent in hydroxy-substituted aromatic compounds, using phenol as an example (see Sect 4.2).



	aromatic species				aliphatic species			
	All data	hydro-carbon	mono-funct.	di-funct.	All data	hydro-carbon	mono-funct.	multi-funct.
# species	66	25	30	11	486	147	215	124
RMSE	0.07	0.06	0.07	0.08	0.15	0.07	0.13	0.22
MAE	0.04	0.03	0.04	0.07	0.09	0.04	0.09	0.16
MBE	0.00	0.02	−0.01	−0.02	−0.02	0.00	−0.02	−0.05

Figure 7: Root mean square error, mean absolute error, mean bias error and box plot for the error distribution in the estimated log k_{298K} values for the full set and subsets of the aromatic species in the database, and for the aliphatic species reported previously (Jenkin et al., 2018a). The bottom and the top of the box are the 25th (Q1) and 75th percentile (Q3), the band is the median value. The whiskers extend to the most extreme data point which is no more than 1.5×(Q3-Q1) from the box. The points are the extrema of the distribution. The black dotted lines correspond to agreement within a factor 2.

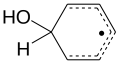
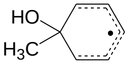
Table 1. Neighbouring group ~~substituent~~ factors, F(X), for α- H-atom abstraction from substituents in aromatics, and their temperature dependences described by $F(X) = A_{F(X)} \exp(-B_{F(X)}/T)$.

Substituent	Parameter	$A_{F(X)}$	$B_{F(X)}$ (K)	$F(X)_{298\ K}$	Comment
$-CH_3$, $-CH_2OX$	F(-Ph1)	8.6	345	2.7	(a),(b)
$-CH_2-$, $-CH<$	F(-Ph2)	7.0	580	1.0	(a),(c)

Comments

[a] The value of F(~~X~~Ph1) or F(Ph2) should be further scaled by the factor "exp(140/T)" for each alkyl group positioned *ortho*- or *para*- to the abstraction group; [b] Applies to H-atom abstraction from CH_3 and CH_2OX substituents. Value of F(-Ph1) is assigned so that k_{prim}.F(-Ph1) equals the recommended H-atom abstraction rate coefficient for the methyl group in toluene, i.e. $2.5 \times 10^{-11} \exp(-1270/T)$ cm^3 $molecule^{-1}$ s^{-1} (IUPAC, 2017a); F(-Ph1) value is also consistent with reported abstraction from the $-CH_2OH$ substituent in benzyl alcohol (Harrison and Wells, 2009; Bernard et al., 2013) and is therefore applied to $-CH_2OX$ groups in general, where -OX denotes the oxygenated groups -OH, -OR, -OOH, -OOR and $-ONO_2$; [c] Applies to H-atom abstraction from secondary ($-CH_2-$) and tertiary (-CH<) groups in ≥ C_2 substituents. Value of F(-Ph2) is assigned on the basis of the reported contribution of H-atom abstraction from the *i*-propyl group in *p*-cymene (Aschmann et al., 2010; Bedjanian et al., 2015).

Table 2. Group rate coefficients for OH addition to carbon atoms in monocyclic aromatic rings, and their temperature dependences described by $k = A \exp(-(E/R)/T)$. Parameters are shown for addition to an unsubstituted carbon (k_{arom}) and to a methyl-substituted carbon (k_{ipso}).

Product radical	Parameter	A	*E*/*R*	$k_{298\ K}$	Comment
		(10^{-12} cm^3 $molecule^{-1}$ s^{-1})	(K)	(10^{-12} cm^3 $molecule^{-1}$ s^{-1})	
	k_{arom}	0.378	190	0.20	(a)
	k_{ipso}	0.378	89	0.28	(b)

Comments

[a] By definition, k_{arom} is ⅙ of the preferred rate coefficient for the reaction of OH with benzene; [b] k_{ipso} at 298 K optimized in conjunction with substituent factors in Table 3, using preferred kinetic data for 12 methyl-substituted aromatic hydrocarbons. The assigned temperature dependence adopts the value of A for k_{arom}, with *E*/*R* adjusted to return the optimized value of k_{ipso} at 298 K.

Table 3. Substituent factors F(Φ) for the addition reactions of OH to aromatic hydrocarbons, and their temperature dependences described by $F(\Phi) = A_{F(\Phi)} \exp(-B_{F(\Phi)}/T)$. Each factor relates to the combination of methyl substitutions indicated relative to the OH attack position (*o-* = *ortho-*; *m-* = *meta-*; *p-* = *para-*).

Number of substituents	Parameter	$A_{F(\Phi)}$	$B_{F(\Phi)}$	$F(\Phi)_{298\,K}$	Comment
1	F(*o*-), F(*p*-)	0.8	-659	7.3	(a)
	F(*m*-)	0.7	-207	1.4	(b)
2	F(*o*-,*o*-), F(*o*-,*p*-)	0.6	-1203	34	(c)
	F(*o*-,*m*-), F(*m*-,*p*-)	2.6	-416	10.5	(d)
	F(*m*-,*m*-)	1.9	-409	7.5	(e)
3	F(*o*-,*o*-,*p*-)	6.8	-760	87	(f)
	F(*o*-,*o*-,*m*-), F(*o*-,*m*-,*p*-)	0.5	-1200	28	(g)
	F(*o*-,*m*-,*m*-), F(*m*-,*m*-,*p*-)	3.5	-341	11	(h)
4	F(*o*-,*o*-,*m*-,*p*-)	2.0	-998	57	(i)
	F(*o*-,*o*-,*m*-,*m*-), F(*o*-,*m*-,*m*-,*p*-)	0.3	-1564	57	(j)
5	F(*o*-,*o*-,*m*-,*m*-,*p*-)	4.7	-809	71	(k)

Comments

Given parameter contributes to the calculation of k_{calc} for the following methyl-substituted aromatics: [a] toluene, *o*-xylene and *p*-xylene; [b] toluene and *m*-xylene; [c] *m*-xylene, 1,2,3-trimethylbenzene and 1,2,4-trimethylbenzene; [d] *o*-xylene, *p*-xylene, 1,2,3-trimethylbenzene and 1,2,4-trimethylbenzene; [e] *m*-xylene and 1,3,5-trimethylbenzene; [f] 1,3,5-trimethylbenzene and 1,2,3,5-tetramethylbenzene; [g] 1,2,3-trimethylbenzene, 1,2,4-trimethylbenzene, 1,2,3,4-tetramethylbenzene, 1,2,3,5-tetramethylbenzene and 1,2,4,5-tetramethylbenzene; [h] 1,2,3-trimethylbenzene, 1,2,4-trimethylbenzene and 1,2,3,5-tetramethylbenzene; [i] 1,2,3,5-tetramethylbenzene and pentamethylbenzene; [j] 1,2,3,4-tetramethylbenzene, 1,2,4,5-tetramethylbenzene and pentamethylbenzene; [k] pentamethylbenzene and hexamethylbenzene.

Table 4. Comparison of estimated and reported branching ratios for H-atom abstraction, $k_{abs}/(k_{abs} + k_{add})$, at 298 K except where indicated.

Compound	Branching ratio		Comment
	calculated	observed	
toluene	6.3 %	6.3 %	(a)
o-xylene	8.3 %	~ 10 %	(b)
m-xylene	3.0 %	~ 4 %	(b)
p-xylene	8.3 %	~ 7-8 %	(b)
1,2,4,5-tetramethylbenzene	6.2 %	(3.7 ± 0.8) %	(c)
hexamethylbenzene	10.8 %	(13.7 ± 4.4) %	(d)
p-cymene (total)	22.4 %	(20 ± 4) %	(e)
p-cymene (at >CH-)	16.2 %	(14.8 ± 3.2) %	

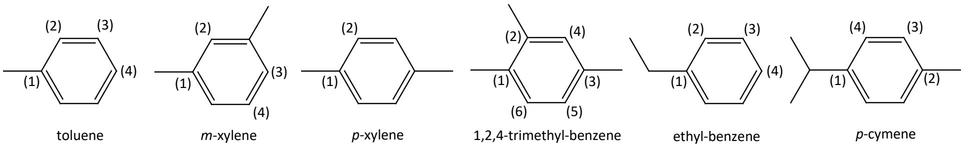
Comments

Sources of observed values: [a] Based on the recommendation of the IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation (IUPAC, 2017a); [b] Calvert et al. (2002); [c] Aschmann et al. (2013); [d] Loison et al. (2012), measurement at 330 K; [e] Taken from Aschmann et al. (2010). Total branching ratio is also consistent with data of Bedjanian et al. (2015).

Table 5. Comparison of estimated branching ratios for OH addition to alkyl-substituted aromatic hydrocarbons at 298 K with those reported in DFT studies. Displayed values are presented relative to k_{add}.

Comment [M1]: This table has been simplified in response to comment by referee 2.

Addition site	Degeneracy	Branching ratios		
1) toluene		This work	Suh et al. (2002)	Wu et al. (2014) [a]
ipso- (1)	1	5.4 %	3 %	16.1 %
ortho- (2)	2	55.9 %	52 %	63.4 %
meta- (3)	2	10.7 %	11 %	5.4 %
para- (4)	1	28.0 %	34 %	15.1 %
2) *m*-xylene		This work	Fan et al. (2008)	Huang et al. (2011) [b]
ipso-, meta- (1)	2	3.5 %	1 %	1.9 %
ortho-,ortho- (2)	1	30.0 %	60 %	60.7 %
ortho-, para- (3)	2	60.0 %	37 %	28.3 %
meta-, meta- (4)	1	6.6 %	2 %	9.1 %
3) *p*-xylene		This work	Fan et al. (2006)	
ipso-, para- (1)	2	32.7 %	20 %	
ortho-,meta- (2)	4	67.3 %	80 %	
4) 1,2,4-trimethylbenzene		This work	Li et al. (2014) [c]	
ipso-, ortho-, para- (1)	1	33.1 %	23.4 %	
ipso-, ortho-, meta- (2)	1	10.2 %	8.5 %	
ipso-, meta-, para (3)	1	10.2 %	5.3 %	
ortho-, ortho-, meta- (4)	1	19.4 %	20.2 %	
ortho-, meta-, para- (5)	1	19.4 %	40.4 %	
ortho-,meta-, meta- (6)	1	7.6 %	2.1 %	
5) ethylbenzene		This work	Huang et al. (2010)	
ipso- (1)	1	5.6 %	6 %	
ortho- (2)	2	56.0 %	53 %	
meta- (3)	2	10.4 %	10 %	
para- (4)	1	28.0 %	31 %	
6) *p*-cymene		This work	Alarcón et al. (2014)	
ipso-, para- (1)	1	17.9 %	18 %	
ipso-, para- (2)	1	14.8 %	3 %	
ortho-, meta- (3)	2	36.8 %	24 %	
ortho-, meta- (4)	2	30.5 %	55 %	



Comments

[a] Values given relative to $k_{add} + k_{abs}$ in Wu et al. (2014), as 15 %, 59 %, 5 %, 14 %; [b] Values given relative to $k_{add} + k_{abs}$ in Huang et al. (2011), as 1.9 %, 60 %, 28 %, 9 %; [c] Values given relative to $k_{add} + k_{abs}$ in Li et al. (2014) as 22 %, 8 %, 5 %, 19 %, 38 %, 2 %.

Table 6. Substituent adjustment factors, R(Φ), relative to the F(Φ) values shown for methyl substituents in Table 3 and k_{ipso} in Table 2. Tabulated values are applicable to 298 K, with suggested temperature dependences provided in the comments [a].

Substituent	Parameter	Position of substituent				comment
		ortho-	*para-*	*meta-*	*ipso-*	
methyl	-	1.0	1.0	1.0	1.0	(b)
ethyl	$R_{\mathrm{et}}(\Phi)$	0.87	0.87	1.0	1.0	(c)
i-propyl	$R_{i\text{-pr}}(\Phi)$	0.83	0.83	1.0	1.0	(d)
n-propyl	$R_{n\text{-pr}}(\Phi)$	0.83	0.83	1.0	1.0	(e)
t-butyl	$R_{t\text{-bu}}(\Phi)$	0.72	0.72	1.0	1.0	(f)
alk-1-enyl (vinyl)	$R_{\mathrm{vinyl}}(\Phi)$	0.0	0.0	0.0	0.0	(g)
-OH	$R_{\mathrm{OH}}(\Phi)$	2.6	2.6	2.4	2.4	(h)
$-CH_2OH$, -CH(OH)R, $-C(OH)R_2$	$R_{\mathrm{C\text{-}OH}}(\Phi)$	3.7	3.7	3.7	3.7	(i)
-C(=O)H, -C(=O)R	$R_{\mathrm{C(O)H}}(\Phi)$, $R_{\mathrm{C(O)R}}(\Phi)$	0.096	0.096	0.096	0.096	(j)
$-OCH_3$, -OR	$R_{\mathrm{OMe}}(\Phi)$, $R_{\mathrm{OR}}(\Phi)$	3.4	3.4	0.79	0.79	(k)
$-OC_6H_5$	$R_{\mathrm{OPh}}(\Phi)$	0.90	0.90	0.21	0.21	(l)
$-C(=O)OCH_3$, -C(=O)OR	$R_{\mathrm{C(O)OMe}}(\Phi)$, $R_{\mathrm{C(O)OR}}(\Phi)$	0.26	0.26	0.26	0.26	(m)
$-NO_2$, $-ONO_2$	$R_{\mathrm{NO2}}(\Phi)$	0.024	0.024	0.070	0.070	(n)

[a] Applied to values of F(Φ) in Table 3 for each component group, and to k_{ipso}; [b] Factors are 1.0 by definition; [c] Based on optimization to data for ethylbenzene, *o*-ethyltoluene, *m*-ethyltoluene and *p*-ethyltoluene. Use of a temperature dependent factor, R_{et}(*o*-) = R_{et}(*p*-) = 0.029exp(1014/T), is provisionally suggested, where the pre-exponential factor is based on that determined for the *i*-propyl group (see comment (d)); [d] Based on optimization to data for *i*-propylbenzene, and *p*-cymene (4-*i*-propyltoluene). Use of a temperature dependent factor, $R_{i\text{-pr}}$(*o*-) = $R_{i\text{-pr}}$(*p*-) = 0.029.exp(1000/T), allows observed preferred temperature dependence of *k* for *p*-cymene to be recreated (see Sect. 3.1.2); [e] Provisionally assumed equivalent to *i*-propyl group adjustment factor, although a much lower factor (0.62) would recreate the reported *k* for *n*-propylbenzene. Use of a temperature dependent factor, $R_{n\text{-pr}}$(*o*-) = $R_{n\text{-pr}}$(*p*-) = 0.029 exp(1014/T), is provisionally suggested (see comment (e)); [f] Based on optimization to data for *t*-butylbenzene. Use of a temperature dependent factor, $R_{t\text{-bu}}$(*o*-) = $R_{t\text{-bu}}$(*p*-) = 0.029 exp(957/T), is provisionally suggested, where the pre-exponential factor is based on that determined for the *i*-propyl group (see comment (e)). [g] Alk-1-enyl (vinyl) substituent is assumed to result in complete deactivation of OH addition to the aromatic ring, based on experimental and theoretical information reported for styrene (Bignozzi et al., 1981; Tuazon et al., 1993; Cho et al., 2014); [h] Based on optimization to data for phenol, 11 methyl-substituted phenols, catechol and 2 methyl-substituted catechols. Use of temperature dependent factors, R_{OH}(*o*-) = R_{OH}(*p*-) = 0.69 exp(395/T) and R_{OH}(*m*-) = R_{OH}(*ipso*-) = 0.025 exp(1360/T) allows a reasonable representation of observed preferred temperature dependences for phenol and cresols. In the absence of data, the parameters are also assumed to apply to -OOH substituents; [i] Based on optimization to data for benzyl alcohol alone, with all factors assumed equivalent. In the absence of temperature dependence data, $R_{\mathrm{C\text{-}OH}}(\Phi)$ = exp(390/T) can be provisionally assumed in each case; [j] Strong deactivation of OH addition by -C(=O)H substituent optimized to recreate dominant (96 %) contribution of H abstraction from -C(=O)H substituent calculated by Iuga et al. (2008), with all factors assumed equivalent. Temperature dependence, $R_{\mathrm{C(O)H}}(\Phi)$ = exp(-698/T), is provisionally assumed in each case which (when combined with those for F(Φ) and k_{ipso}) results in a weak overall temperature dependence, consistent with calculations of Iuga et al. (2008). Factors also assumed to apply to -C(=O)R substituents; [k] Based on optimization to data for methoxybenzene and 1,2-dimethoxybenzene. Use of R_{OMe}(*o*-) = R_{OMe}(*p*-) = exp(365/T) and R_{OMe}(*m*-) = R_{OMe}(*ipso*-) = exp(-70/T) leads to overall weak negative temperature dependence near 298 K, consistent with data of Perry et al. (1977) over the range 300-320 K. Factors assumed to apply to -OR substituents in general (with the exception of -OPh groups), and are also assumed to apply to -OOR substituents in the absence of data; [l] Based on optimization to data for diphenyl ether alone, by scaling the optimized values of $R_{\mathrm{OMe}}(\Phi)$; [m] Based on optimization to data for methyl salicylate alone, with all factors assumed equivalent. In the absence of temperature dependence data, $R_{\mathrm{C(O)OMe}}(\Phi)$ = exp(-400/T) can be provisionally assumed in each case. Factors assumed to apply to -C(=O)OR substituents in general; [n] Based on optimization to data for nitrobenzene, 1-methyl-3-nitrobenzene and four methyl-substituted 2-nitrophenols (with values of $R_{\mathrm{OH}}(\Phi)$ applied, where appropriate). In the absence of temperature dependence data, R_{NO2}(*o*-) = R_{NO2}(*p*-) =exp(-1110/T) and R_{NO2}(*m*-) =R_{NO2}(*ipso*-) = exp(-792/T) can be provisionally assumed. Parameters are

also assumed to apply to -ONO_2 substituents, in the absence of data.

Table 7. Partial rate coefficients for the reactions of O_2 with OH-aromatic adducts, and their temperature dependences described by $k = A\exp(-(E/R)/T)$. Parameters are shown for abstraction of hydrogen α- to the -OH group ($k_{abs\text{-}O2}$) and the reference rate coefficient for β- O_2 addition adjacent to the -OH substitution ($k°_{add\text{-}O2}$).

Parameter	A	E/R	$k_{298\ K}$	Comment
	(10^{-14} cm^3 molecule^{-1} s^{-1})	(K)	(10^{-17} cm^3 molecule^{-1} s^{-1})	
$k_{abs\text{-}O2}$	1.75	1500	11.4	(a),(b)
$k°_{add\text{-}O2}$	1.50	1700	5.0	(b),(c)

Comments

[a] Value of E/R based on the activation energy calculated for H atom abstraction from the OH-benzene adduct by Raoult et al. (2004); [b] Value of A for k_{abs} and of $k°_{add}$ at 298 K optimized so that $k_{abs} + 2k°_{add} \approx 2.1 \times 10^{-16}$ cm^3 molecule^{-1} s-^{1}, and $k_{abs}/(k_{abs} + 2k°_{add}) \approx 0.53$ at 298 K, consistent with IUPAC recommendations (www.iupac.pole-ether.fr) and the literature; [c] Value of A for $k°_{add}$ set to be consistent with calculations of Raoult et al. (2004), with E/R automatically returned from A and the 298 K value of $k°_{add}$.

Table 8. Substituent factors $F_i(X)$ for the addition of O_2 to aromatic adducts reactions of OH to aromatic hydrocarbons, and their temperature dependences described by $F_i(X) = \exp(-B_{Fi(X)}/T)$.[a]

Location of substituent [b]	Parameter	$B_{Fi(X)}$	$F_i(X)_{298\ K}$
1	F_1(-alkyl)	0	1.0
2	F_2(-alkyl)	-207	2.0
3	F_3(-alkyl)	-620	8.0
4	F_4(-alkyl)	-207	2.0
5	F_5(-alkyl)	-558	6.5

Comments

[a] Values of $F_i(X)_{298\ K}$ optimized to recreate the trend in yields of hydroxyarene (phenolic) products for toluene, *m*-xylene, *p*-xylene, 1,2,4-trimethylbenzene and 1,3,5-trimethylbenzene (see Table 3). The values are therefore based on data for methyl substituents, but are assumed to apply to alkyl substituents in general. Values of $B_{Fi(X)}$ assume that the temperature dependence of $F_i(X)$ can be described by $\exp(-B_{Fi(X)}/T)$; [b] As shown in Fig. 3 and discussed in Sect. 4.1.

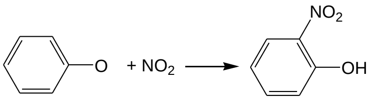
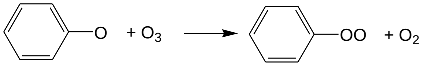
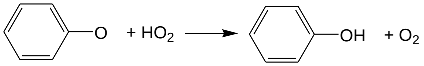
Table 9. Substituent factors, $F_a(X)$ and $F_b(X)$, for addition of O_2 to stabilized peroxide bicyclic radicals. Parameters shown are for 298 K, but are assumed to apply to the atmospheric temperature range [a].

Substituent	$F_a(X)$	$F_b(X)$	Comment
-H	1	1	-
alkyl	1000	3	(b),(c)
oxygenated substituents	see comment		(d)

Comments

[a] Factors related to addition of O_2 at positions 'a' and 'b' in Fig. 4 as discussed in Sect. 4.1; [b] Activating effects of alkyl substituents are informed by calculations for structures formed in the toluene system by Wu et al. (2014) and in the 1,2,4-trimethylbenzene system Li et al. (2014), with a particularly strong effect for substitution at position 'a'. The assigned values were optimized to allow a reasonable representation of the relative yields of α-dicarbonyl products from methyl-substituted aromatics (see Sect. 4.1, Fig. 5 and Table S2). The values are therefore based on data for methyl substituents, but are assumed to apply to alkyl substituents in general; [c] Also applied to substituted alkyl groups not covered by comment (d); [d] If the resonant peroxide bicyclic radical contains an oxygenated substituent at either or both positions 'a', addition of O_2 is assumed to occur exclusively at the site possessing the substituent that is higher in the following list: -OH/-OR/-OOH/-OOR > -OC(=O)H/-OC(=O)R > alkyl/-H > -C(=O)H/-C(=O)R > -C(=O)OH/-C(=O)OR > $-ONO_2$ > $-NO_2$. If both sites possess a substituent of the same rating, O_2 addition is assumed to occur equally at each site.

Table 10. Reactions represented for phenoxy and substituted phenoxy radicals, and their assigned rate coefficients (in units cm^3 $molecule^{-1}$ s^{-1}).

Reaction	Rate coefficient	Comment
	1.0×10^{-12}	(a)
	2.9×10^{-13}	(b)
	2.3×10^{-13}	(c)

Comments

[a] Rate coefficient per unsubstituted *ortho*- site, based on that reported for C_6H_5O by Platz et al. (1998), and assumed to apply over the tropospheric temperature range; [b] Rate coefficient based on that reported for C_6H_5O by Tao and Li (1999), and assumed to apply over the tropospheric temperature range The products of the reaction were not characterized and are assumed here; [c] Represented on the basis of evidence reported by Jenkin et al. (2007;2010) and Herbinet et al. (2013) (see Sect. 5). In the absence of kinetics determinations, the rate coefficient is assumed equal to that calculated for the reaction $CH_3O + HO_2 \rightarrow CH_3OH + O_2$ by Mousavipour and Homayoon (2011), which is reported to be insensitive to temperature over the range 300-3000 K .