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 Jenkin et al., ACPD, 2018

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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.

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.

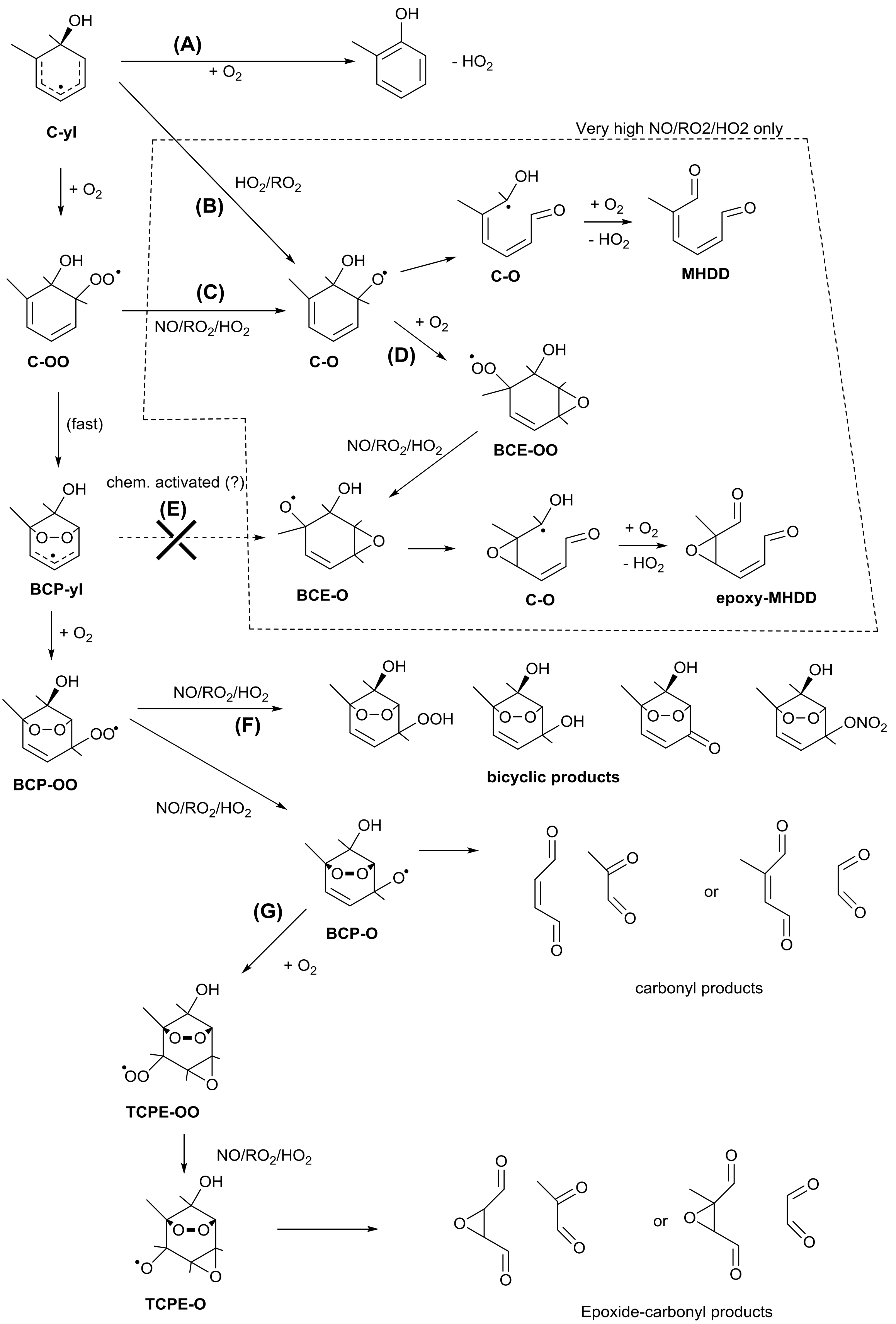

Figure LV-1 : Extended mechanism for aromatic oxidation (toluene used as example). Stereo- and site-specificity is ignored.

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).

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.

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.

(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.

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.

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.

The O_2-dependence of the **MHDD** yield in NO-free conditions (fig. 5, Birdsall and Elrod 2011) suggests that both the **C-yl** + RO2 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 RO_2-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 $\sim 10^3$ 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 O2, 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 O2, versus lowering C-O formation by **C-yl** to **C-OO** capturing by O2. 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 O2-dependence is thus consistent with alkoxy radical epoxidation.

On the other hand, the O2-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 O2 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.

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.

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 RO2+RO2 rate coefficient for allyl-peroxy radicals was measured at $7x10^{-13}$ cm3 s-1 ((Jenkin et al., 1993), with rate coefficients for other RO2 radicals + NO lower than this (Orlando and Tyndall, 2012). With a **BCP-OO**+NO rate coefficient of 7.7E-12 cm3 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 O2 addition. The rate coefficient for **C-yl** + O_2 has been determined at ~10^{-13} to 10^{-16} cm3 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 [O2] from 5E17 to 6E18 cm-3 as in Birdsall et al. 2010 yields a pseudo-first order kO2 ~ 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** + RO2/HO2 it could instead break the weak OO bond in the C-OOR product. Either way, at least [RO2/HO2] 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+RO2) = 5x10-12 cm3 s-1 then requires [RO2/HO2] ~ 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 [RO2] 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.

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.

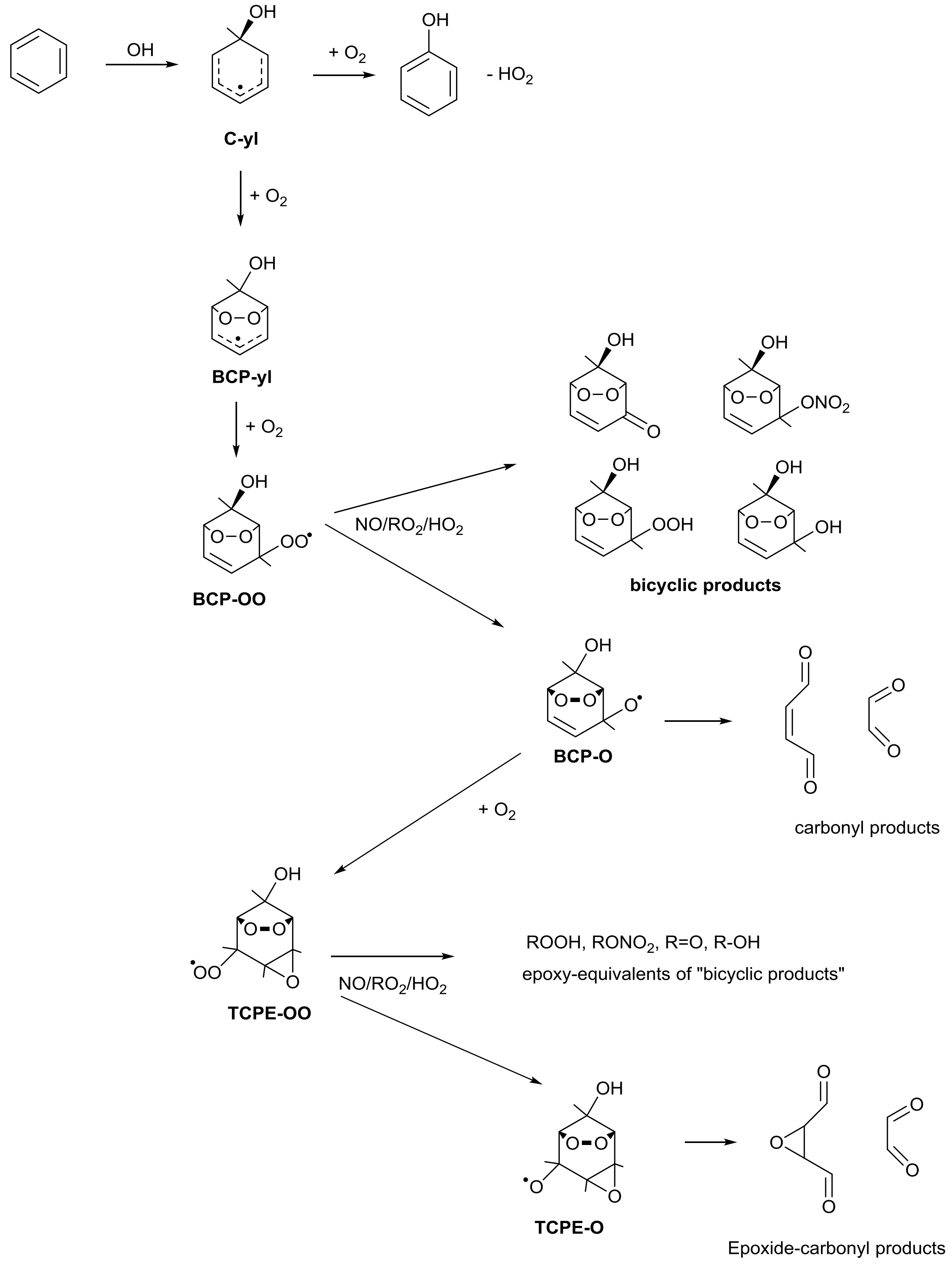

Figure LV-2: Reduced mechanism for aromatic oxidation under atmospheric conditions (stereo- and site-specificity ignored).

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