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Atmospheric Chemistry and Physics Discussions

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Interactive comment

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.

Anonymous Referee #1

Received and published: 15 March 2018

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

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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.

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).

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

Below, are some specific comments:

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.

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.

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.

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

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.

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

. . .and some 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)

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”.

Table 8: check the title. Page 12, line 10: replace reference to Fig. 4 with Fig. 3

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