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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 #2

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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

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Discussion paper

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.

Specific comments

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.

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?

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.

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

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. Additionally, on what theoretical grounds might these adjustments be justified?

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

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.

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

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?

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?

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.

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