

Interactive comment on “Predicting arene rate coefficients with respect to hydroxyl and other free radicals in the gas-phase: a simple and effective method using a single topological descriptor” by M. R. McGillen et al.

Anonymous Referee #2

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The paper by McGillen et al describes the use of a topological descriptor for prediction of rate coefficients for reactions of a range of radicals with arenes. The method is simple and successfully predicts arene reactivity towards OH and O(3P). The paper is well written and provides interesting insights into trends in reactivity. The authors already published several papers using essentially the same approach and the research presented is thus merely an extension of previous work. However, the simplicity of the method might make it attractive for researchers who need a quick idea for the value of a rate constant. The manuscript merits publication mainly because of this potential

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application in atmospheric modelling.

My main criticism concerns the modelling section in the manuscript. I believe in its current form this section does not add significant value to the paper and the figures provided are not very insightful. More details and explanations should be given about the input parameters and choice of model (references to the emission inventory used and the National Atmospheric Emissions Inventory; absolute values for NO_x concentrations; most importantly an indication of the complexity of the model: how many other reactions are considered and what is the contribution to the total concentration profiles of those reactions where the rate constants differ significantly between Calvert et al and the predicted values presented in the paper; what is the 'reduced mechanism similar to CRI' and in which way does it differ from CRI?). It remains unclear how large is the impact of the arene reactions on the concentration profiles shown in the figures, so that it is not possible to evaluate the influence of the different rate parameters used. A potentially interesting modelling project is suggested at the end of the modelling section (using the full mechanism with the newly predicted rate data), but unfortunately not performed. The conclusion reached by the authors that the omission of minor species is likely to lead to the main uncertainty in the model output indicates that the modelling study should also to be performed with the full mechanism. I suggest either to remove the modelling section from the paper or to perform the modelling study also with the full mechanism for comparison and identify the relative contributions of the arene reactions to the different concentration profiles.

Specific comments:

The authors swap between correlation coefficient, r^2 and R^2 which should be avoided. AQIRP, 1995 is not identified in the references.

A reference is missing for electron density calculations of alkenyl substituted arenes.

The OH dataset only extends over two orders of magnitude and I do not think that the

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OH dataset is necessarily the most insightful (stated in the first paragraph in discussion section), since the ranges of reactivities are much larger for other species e.g. for NO₃ (seven orders of magnitude).

It should be mentioned that the similarity between the reactivity of OH and O(3P) has already been shown in 1990 by Wayne et al.

It would be desirable to give references to the original papers for the rate constants rather than referring to the NIST online database which is known to contain numerous errors.

What is the meaning of superscript 20 and 21 in table 3?

Interactive comment on Atmos. Chem. Phys. Discuss., 7, 2961, 2007.

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