

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.

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We thank the referee for their helpful and positive comments. The referee makes the point that quite a lot of data are required in order to establish trends between molecules containing different numbers of primary, secondary, etc. carbon atoms. These concerns are valid in the sense that molecules containing different total numbers of primary (1°), secondary (2°) and tertiary (3°) carbon atoms (referred to in the article as sigmas $x^\circ x$) occupy separate trendlines, and that the greater the number of data points in each trendline, the more reliably the parameters of Equation II can be constrained. This limitation is discussed in the article with reference to the less populous O(3P)

dataset (pp. 2969-70). However, the authors would like mention that this is a limitation common to most highly discriminating structure-activity relationships (SARs), since they are reliant upon measured data, often from classes of compounds that are poorly represented; notwithstanding, the topological approach is not expected to be adversely affected, since the tunable parameters used in Equation II are adjusted to optimize the correlation of the entire dataset and as a result, bias introduced by the scatter of a small subgroup remains minimal.

In response to the referee's queries on temperature-dependence, the authors can confirm that the number of temperature-dependent kinetic measurements of arene-radical reactions is extremely limited. A quick consultation of the literature yielded 6 temperature dependent measurements of arene-OH kinetics at a comparable temperature range (800 K), notably benzene, toluene, p-xylene, o-xylene, m-xylene and ethylbenzene. This is not considered sufficient for a reliable SAR estimate, however, a strong correlation was observed for the 5 members of the sigma x^o subgroup, possessing a correlation coefficient of 0.99. The referee makes an interesting point about the possibility of an increasingly important abstraction channel at higher temperatures. The authors agree that this is a distinct possibility, and suggest that the form of Equation II would afford flexibility of the SAR in this regard (e.g. spacing between sigma x^ox subgroups would be expected to decrease at elevated temperatures, which could be accounted for by adjusting the tunable parameters of Equation II). Although it is acknowledged that in the absence of a larger temperature dependent dataset, this assertion is rather conjectural at present. Regarding the suggestion that analogies could be drawn between arene and alkene temperature-dependent reactivity: unfortunately, the number of temperature-dependent measurements of alkene reactions is similarly small and because of this, the authors are not confident in drawing such an analogy.

As the referee suggested, the authors have now read the paper by D. Grosjean. It is stated in this paper that the reaction of styrene with OH proceeds by addition to the olefinic bond, although this statement does not refer to any previous study or support-

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ing evidence. Major products were found to include benzaldehyde, formaldehyde and PBzN. Detection of these products is concordant with the above statement, unfortunately, product yields for benzaldehyde are absent, and it is unclear as to whether or not the products of the remaining oxidation pathways could be quantified even if they were present.

In the worked example of indene, vertices 5 and 1 appear twice in the equation for the Randic; index because in the graph of the resonance structure of this compound, there is a double bond between these two vertices, which corresponds to two edges. The referee's attention is drawn to vertices 2 and 3, 6 and 7, and 8 and 9, which also appear twice and represent the three remaining double bonds contained within this Kekulé structure.

The referee expresses some doubt about the applicability of using the SAR estimates in the CRI mechanism, the main concern relating to the CRI being insensitive to arenes. If the referee is asserting that arenes are not important (don't think this is the case) then the authors disagree with this and would recommend reading the following papers:

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.

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.

Derwent et al. (1996) reported a list of 50 VOCs which were ranked in order of their potential to form ozone through photochemical processes and took into account their respective emission fluxes. In this list, toluene ranked 1st, with m-, p- and o-xylenes ranking 4th, 5th and 6th respectively, and with many other arenes present throughout this list. The authors therefore consider the MCM to be highly sensitive to error within arene rate coefficient measurements/ estimates.

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However, we believe that the referee is asking a different question, in a manner similar to the other referee of this paper. We wanted to check what impact the differences in rate coefficient determined by the SAR developed in this work and measured data had on ozone and other species. It is often the case in papers developing SARS that authors state that the SAR agrees well (plus or minus 50

In response to the remark that the referee would be more convinced by the applicability of the method if estimates were compared with new measured data, the authors would like to clarify our intentions. By implementing estimated rate coefficients in the CRI mechanism, we intended to validate the utility of the SAR in atmospheric modelling. We did not intend to validate the SAR's predictive abilities, of which we are already confident, given the strength of the correlations reported in the paper. The authors would gladly pursue this latter objective for the sake of thoroughness if resources would allow it, alas, at present, they do not.

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

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