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Atmospheric
Chemistry
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Discussions

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 #1

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The paper describes a novel method a Randic-type topological index for predicting arene rate coefficients. The approach is new, simple and appears to be an effective way of predicting arene reactivity toward OH and O(3P) radicals, at least for alkyl- and alkenylbenzenes by room temperature. One disadvantage that I see with the method is that quite a lot of data is necessary in order to establish trendlines for molecules with different numbers of primary, secondary etc carbon atoms. Have the authors tried to apply the approach for temperatures other than room temperature? There is probably not very much temperature dependent kinetic data available for the arenes but there

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might be enough to judge whether or not the method will function at other temperatures. If it works at other temperatures this would make the approach very valuable. Lack of temperature dependent kinetic data is a major problem when modeling the chemical processes in the different atmospheric regimes. Many of the aromatic hydrocarbons show a complex temperature dependence with abstraction from alkyl substituents becoming increasingly more important with increasing temperature. Perhaps the authors have tried this for the alkanes and alkenes and could make some comment. I also find it surprising that alkenyl substituted arenes fit seamlessly into the ?xoo trendline for the OH reaction, I was also equally surprised that no product has been made that would answer where the OH is actually going. I made a quick literature search and came up with the paper of Tuazon et al. Environ. Sci. Technol. 27(1993)1832-184, which gives products for the ozone and NO3 reactions but not the OH oxidation. I also found a paper:

D. Grosjean, Atmospheric reactions of styrenes and peroxybenzoyl nitrate. Science of the Total Environment, 46(1985)41-59.

Unfortunately I do not have access to this journal. I advise the authors to check out the paper, perhaps there is some product information in it. In the worked example of the Randic index for indene “5 and 1” appears twice in the equation. Is this because it is a bridged compound? Perhaps a word of explanation here would not go amiss. Perhaps using “1 and 5” and “5 and 1” might be better. For the other readers of the paper the McGillen et al. (2006b) reference has now been published: Chemosphere 65, 2035-2044 (2006). The authors have used a simplified version of the MCM to test the performance of the predicted rate coefficients against the actual experimental values. The comparison is reasonable. I am not really very convinced by this exercise since in such a large mechanism the outcome will probably not be very sensitive to relatively minor differences in the rate coefficients. Even if two or three of the rate coefficients are wrong by an order of magnitude I do not suspect that the change in the model outcome will be significantly affected unless the substances in question have high concentrations. I would be considerably more convinced by the power of the method if the authors used the method to predict rate coefficients for arene species not yet measured and then proceeded to have the values experimentally verified either by themselves or by some other group.

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