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Atmospheric Chemistry and Physics 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.

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We thank the referee for their positive comments and note their misgivings with respect to the usefulness of the atmospheric modelling section. On reflection we agree that this section ought to be presented more clearly and in doing so, hope to have addressed the referee's concerns regarding the basic details of the model. The mechanism used was the CRI and we have amended this in the text to avoid confusion. We performed some integrations with the full MCM mechanism at the start of this study and there was no change in the concentrations retrieved using either mechanism. Since the CRI is far quicker to run we decided to use this mechanism for the full analysis.

We believe that this is a useful exercise and a useful addition to the paper since 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. From this analysis it is clear that the change in rate coefficients from the recommendations of Calvert (2002) to those predicted in this study has no impact on ozone, NOx, HOx etc. and that the only species where there is a discernible difference is HCHO and PAN (3-5% maximum)

It is often the case in papers developing SARs that authors state that the SAR agrees well (plus or minus 50% say) and leave it at that. It has been our experience that for some of these systems, tolerances that are deemed to suggest 'good agreement' are in fact an unacceptable tolerance and that that difference has a significant impact on the concentrations derived from the model. Therefore we wanted to assess the predicted rate coefficients and confirm that the agreement provided by the SAR did not affect model concentration. The revised text is given below.

5. Atmospheric implications

The impact of using rate coefficients estimated through our method versus the recommended values of Calvert et al. (2002) upon the output of an atmospheric model was assessed. The model has been described in detail before (Utembe et al., 2005) and uses the CRI mechanism described in detail by Jenkin et al., 2002. Initial comparisons were made using the full MCM mechanism and the CRI mechanism, where it emerged that the two mechanisms yielded the same results. The reduced mechanism was therefore adopted for the complete set of integrations, since it is more efficient to run. Briefly, the model was integrated for four days using a Gear type solver. Emissions of NOx, CO, SO2, CH4 and some 124 VOCs (detailed in previous papers) were incorporated into the model using the National Atmospheric Emissions Inventory (NAEI) (http://www.naei.co.uk). The box model was assumed to be static in space but was subjected to diurnally varying emissions, deposition (where this had a diurnally varying component), temperature and sunlight. A range of NOx conditions appropriate to

ACPD
7, S1810–S1814, 2007

EGU

the urban environment were required for this study, the NOx emissions were scaled by factors of 0.1, 0.5, 1.0, 2.0, and 3.0 and covered NOx concentrations from around 500 ppt through to 20 ppb.

Rate coefficients of arenes with respect to OH were obtained from measurement data as recommended by Calvert et al. (2002). The rate of change of each arene is dependent on its initial concentration, the level of emission, and the concentrations of atmospheric oxidants (mainly NO3 and OH).

The reduced mechanism was restricted to arenes with 8 or less carbon atoms, therefore the list of arenes for which rate coefficients were altered are: benzene, toluene, p-xylene, o-xylene, m-xylene, mesitylene, hemimellitene, psi-cumene, styrene, ethylbenzene, p-ethyltoluene, o-ethyltoluene, m-ethyltoluene, cumene, and n-propylbenzene. Figure 7 shows that over the whole range of NOx conditions, our rate coefficients estimates have a minor effect upon the modelled mixing ratios of ozone in comparison with those obtained from using measurement data. Altering the rate coefficients between those predicted in this work and those recommended by Calvert et al. (2002) have a small impact on the relative rate of ozone production arising from the oxidation of these arenes (around 15-20%) and have a negligible impact on the absolute rate of production ($<$5%). The reason for the small impact on the absolute rate of production is that for those key arenes that contribute most to ozone formation (either because they are the highest emission or the fastest rate coefficient or both), the agreement between predicted and measured is very good (typically within 20%). Furthermore, only minor effects were observed upon the concentrations of other major species (such as NOx and HOx), especially under conditions of low NOx. Differences in the concentrations of other important species e.g. formaldehyde (HCHO) and peroxyacetyl nitrate (PAN) mixing ratios only began to emerge at NOx emission factors greater than 1.0, where the difference was 3-5% at the most.

Further modelling studies were conducted to compare the estimates using the topological approach with those predicted using the method proposed by Zetzsch. As

ACPD

7, S1810–S1814, 2007

Zetzsch's method does not include alkenyl substituted arenes, the rate coefficient of styrene was not altered. The results suggest that rate coefficients predicted by the topological approach compare with measured values as well as, if not better than the values predicted by Zetzsch. The differences between the method of Zetzsch and the topological approach become most apparent for [PAN] and [HCHO] under high NOx conditions (see Figure 8).

We conclude that the topological approach is a most suitable method for predicting such rate coefficients for inclusion in chemical mechanisms such as the MCM. It is further suggested that there are many species of arene for which kinetics with respect to atmospheric oxidants are not available that are present in vehicle exhaust emissions (e.g. AQIRP, 1995) and which therefore are of potential importance in urban environments, and it is probable that failure to account for these minor species will result in a greater error associated with model output than the error associated with the use of modelled versus measured rate coefficient data.

Utembe, S.R., Jenkin, M.E., Derwent, R.G., Lewis, A.C., Hopkins, J.R., Hamilton, J.F. Modelling the ambient distribution of organic compounds during the August 2003 ozone episode in the southern UK. Faraday Discussions 130, 311-326 (2005).

In response to the minor points raised by anonymous referee #2:

Inconsistency between R2 and r2 is noted and has been amended in the text.

A full reference for (AQIRP, 1995) has been added to the list of references.

References for the electron density calculations have also been added to the list of references.

In response to the referee's assertion that the OH dataset is not necessarily the most insightful on the grounds that the range of reactivity exhibited by this dataset is dwarfed by the NO3 dataset, the authors were rather alluding to the range of conformations afforded by the OH dataset. Many of these conformations belong to Σx°x groups

ACPD

7, S1810–S1814, 2007

that are scarce or nonexistent in the other datasets, and the authors therefore consider the OH dataset to be particularly instructive in this regard.

We have, as suggested by the referee made refernce to Wayne et al., 1990.

A full list of references for the rate coefficients contained within this work has been added to the manuscript.

Superscripts 20 and 21 represent typographical errors and have been substituted for the references to the literature.

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