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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Modelling the evolution of organic carbon during its gas-phase tropospheric oxidation: development of an explicit model based on a self generating approach" *by* B. Aumont et al.

Anonymous Referee #2

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General Comments

The paper presents the approach taken in the development of a computer program, "generator", which produces explicit gas phase oxidation reaction schemes under tropospheric conditions, for acyclic volatile organic compounds. It represents an important and significant development in the field of computer generated reaction mechanisms for use in tropospheric chemistry models. The extensive details of reference material used, assumptions made, and discussion of decisions in implementation of various

strategies is beyond the scope of a journal article, and needs to be made available elsewhere, possibly through a web interface. The authors carry out simulations under typical tropospheric conditions, using a mechanism produced by their "generator" approach, and present some comparisons with other mechanisms already available in the literature (SAPRC99 and MCMv3). It is becoming increasingly important to be able to make use of the very extensive literature data bases concerning atmospheric reaction kinetics, and products and branching ratios data, together with currently available SAR recommendations, to be able to probe the chemistry beyond simulation of ozone profiles. Such computer generated schemes are the only realistic way to generate fully explicit degradation mechanisms, however because of the large number of assumptions required it is also important to test the generated schemes as rigorously as possible. This paper presents a good first step in this testing, though it would have been useful to have some extension of the work presented to address the questions of limitations of the current "generator" code. The final section on an example of how this type of mechanism code can be used to follow the developing organic budget, and possible extension to aerosol developments is an indication of the potential of such tools to extend our understanding of the highly complex and multiphase atmospheric system. I recommend it for publication after addressing the specific comments and technical errors detailed below.

Specific comments

If no additional model work is available on a larger range of VOC (for example highly branched species), the abstract should remove the reference to "organic compounds" and replace this with a term that more accurately describes the class of compounds for which the generator is able to produce oxidation mechanisms.

There is overall general description of using literature measurements where available and SAR otherwise, but no clear discussion of how this applies to the examples provided. Some determination of the sensitivities of the model outputs to significant rate coefficients and branching ratios would be useful.

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In the evaluations section the authors state no numerical bias on integration of the generator schemes (10ˆ5 species and 10ˆ6 reactions). It would be useful to know the time differences on running the different models.

Here also some analysis of why the different approaches (generator, SAPRC99 and MCMv3) lead to the largest differences in some of the secondary products presented HCHO, methyl glyoxal and PANs would be useful, and what is different about the 2 examples given that leads to a larger discrepancy in HCHO for heptane than isoprene for the SAPRC99 code??

Technical corrections

In general the paper is well written, however these were quite a few typographical errors which should be corrected. Corrections are given in capitals.

p.705 l.14 associated WITH high Henry's Law coefficientS p.706 l.8 detaileD p.706 l.25 mechanimS p.707 l.3, l.14 mechanimS p.708 l.16 be already, change to ALREADY BE p.709 l.23 avoid the use of repeated full stops p.710 l.13 identified should be IDENTIFY p.716 l.3 provided IN Table 2 p.716 l.20 positionS (and also) factor OF p.718 l.4 Rate constantS p.719 l.4 Rate constantS p.720 l.2 THE branching ratio p.720 l.13 decompositionS p.723 l.16 size AS the p.724 l.12 previously STATED p.725 l.19 detail (no plural s) p.726 l.1 Answering THESE

Table 8 caption. The caption should more clearly indicate what the authors mean by significantly. State what proportion these species represent.

Figure 6 legend. Here are the visual images of the comparisons of the various mechanisms used. The chart for METHYL GLYOXAL is misleading in that only 2 lines are present, and though this is described in the text, the chart or legend should indicate that the SPARC99 mechanism for heptane does not include METHYL GLYOXAL.

Interactive comment on Atmos. Chem. Phys. Discuss., 5, 703, 2005.