

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.

B. Aumont et al.

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We would like to thank the referee for the comments

General comments

> The authors need to make a comprehensive report describing the method in detail available on the Internet, and include a reference to it in this manuscript.

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As stated by the referee, it is impossible to comprehensively describe in a journal article of reasonable size the methods and the database used to develop the generator. However, the methods are fully described in a PhD thesis (Sophie Laval-Szopa, 2003). The reference to the thesis is given in the paper as well as a link to download it. The thesis is in French but the data in the tables should be understandable. A report (in English) describing the method in detail is under preparation and will be made available on the web.

> Calculation results are given only for n-octane and isoprene. It would have been of interest to see how the results compared with those for MCM and more condensed mechanisms for a larger varied of compounds.

It should be very interesting to compare the "predictions" of various schemes for a larger set of precursor (e.g. alkanes, branched alkanes, terminal alkenes, internal alkenes, conjugated double bonds species, ethers ...). However, a systematic comparison of various schemes was beyond the scope of the paper and, as suggested by the referee, additional papers will be written for that purpose.

Specific comments

> It seems to me that it would be more accurate to state that it is applicable to "acyclic hydrocarbons and their oxidation products".

Yes. The abstract is changed to include this suggestion in the revised version. The reason for (currently) excluding cyclic species is not scientific, but stems from technical coding issues in generating unique names for all molecules (those initially specified and as well as those which are computer-generated),

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which for cyclic compounds requires particular attention to avoid duplicities. This coding limitation will be removed in the near future.

> It is stated that it cannot handle cyclic compounds (except by manual input), but it can handle isoprene. Can it handle compounds and radicals with more than one double bond? Unsaturated radicals can undergo many types of reactions that are probably not considered and are difficult to estimate.

The generator can handle species with two $>C=C<$ bonds (conjugated or not). For conjugated $C=C$ bonds, 1-2 and 1-4 additions are considered in the generator. Furthermore, the $>C=C<$ bond can be conjugated with carbonyl groups. More generally, each radical structure produced by a reaction is checked by a generator subroutine. If the radical possess delocalized electrons (or an "atypical" structure), the subroutine returns the "preferred" structures. For example, if a reaction pathway lead to the formation of a $>C=C(O)\cdot$ radical, the "radical check" subroutine returns a $>C(\cdot)-CO\cdot$ structure. It is clear that rate constants (or branching ratio) are difficult to estimate for many reactions and the choices performed for few reaction types are rather arbitrary. We would like to emphasize that the generator is only an expert system that "assimilate" data or parameterization (e.g. rate constants, structure/activity relationships, branching ratios, thermo dynamical data ...) and use them to provide update chemical schemes. The generator uses only empirical data or parameterization (i.e. SAR) ; it cannot provide estimate based on more fundamental approaches (e.g. ab initio). The paper is revised to provide more specific information concerning the types of molecules the current version of the generator can handle (page 709, line 25).

> Many radicals, and products, particularly the highly substituted radicals that

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occur after several generations of reactions, have groups for which no group thermochemical estimates are given by Benson. How are these cases handled?

In addition to Benson data, we used the group estimates provided by Carter (2000). This reference is added to the revised manuscript (page 742, footnote of table 6). We estimate few additional groups. Group data used for the present study can be found in Laval-Szopa (2003) thesis, Appendix 2, page 195.

> *Kirchner et al (1997) and Christensen et al (1999) reported synthesizing CH₃OC(O)OONO₂ from the reaction of Cl₂ with methyl formate, which is only possible if CH₃OC(O). lasts long enough to react with O₂ to form CH₃OC(O)OO.*

Yes. The generator will be updated and we performed the necessary revision in the manuscript (suppress the corresponding line in table 1, O₂ addition being the general case for -CO(.) structure).

> *Nowhere in this work is it mentioned that Carter (2000) also developed an automated mechanism generation system, though it is not as comprehensive as the one described in this work.*

The reference to Carter (2000) is added (line 9, page 108).

Technical Corrections

The suggested corrections are performed in the revised version of the paper

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