

***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 #1**

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General Comments

This paper describes an automated method to generate fully explicit mechanisms for the atmospheric reactions of acyclic hydrocarbons and their oxidation products. This is probably the only practical way to generate explicit mechanisms for atmospheric reactions medium size and larger molecules, and explicit mechanisms are ultimately necessary to relate the condensed mechanisms used in airshed models to basic laboratory data. The approach employed follows the method developed by Carter (2000),

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but extends it by generating the mechanism for all the oxidation products as well as the parent compound, and actually conducts model simulations with mechanisms with tens or hundreds of thousands of reactions. This type of work is of fundamental interest to atmospheric chemistry. Although as this paper shows the fully explicit mechanism probably isn't necessary for ozone predictions, I agree with the authors conclusions that this approach is necessary for assimilating experimental data and estimation methods in a consistent and comprehensive manner and that this will be a valuable tool for developing predictive models for SOA formation that are based on actual chemistry.

The amount of assumptions and detail that goes into this work is extensive and it is impossible to comprehensively describe in a journal article of reasonable size the method and, estimation methods, and measured rate constant and branching ratio database that must go into the method. For that reason, it is impossible to review the full scientific merits of everything that goes into this work. Something the size of the Carter (2000) report would be needed to describe the method sufficiently so that it can be reviewed and utilized by other researchers. 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. However, the journal article is valuable in making aware of this work and the results that can be obtained.

The examples provided are limited to the n-alkanes through octane and isoprene, and 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. Interesting comparisons would have been predictions of ozone, OH, NO<sub>x</sub> species, and general types of organic functional groups. Hopefully this, and the application of the method to evaluating condensation approaches, will be discussed in subsequent papers from this group.

More discussion of the limitations of the method and those cases where it may not give appropriate estimates may probably be appropriate.

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## Specific Comments

The abstract states that the paper describes a tool for developing explicit mechanisms for “organic compounds”. It seems to me that it would be more accurate to state that it is applicable to “acyclic hydrocarbons and their oxidation products”. In this regard, the body of the paper should give more specific information is needed concerning the types of molecules the generator can and cannot handle. 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.

It is stated that the estimations for the rate constants for most of the alkoxy radical reactions are based on estimation methods of Carter (2000), many of which require estimated heats of reaction, derived using group-additivity methods of Benson (1976). Heats of reaction estimates are also required for other estimates. However, many radicals, and products, particularly the highly substituted radicals that occur after several generations of reactions, have groups for which no group thermochemical estimates are given by Benson. How are these cases handled?

Table 1 indicates that they assume that radicals of the type R-O-C(O). rapidly decomposes to R. + CO<sub>2</sub>. However, Kirchner et al (1997) and Christensen et al (1999) reported synthesizing CH<sub>3</sub>OC(O)OONO<sub>2</sub> from the reaction of Cl<sub>2</sub> with methyl formate, which is only possible if CH<sub>3</sub>OC(O). lasts long enough to react with O<sub>2</sub> to form CH<sub>3</sub>OC(O)OO. This is discussed by Carter (2000), who assumes that the O<sub>2</sub> reaction dominates. However, this is probably not important for the specific compounds discussed in this paper.

Since this builds to a large extent on the work of Carter (2000), a discussion of differences between this work and that would be appropriate. Nowhere in this work is it mentioned that Carter (2000) also developed an automated mechanism generation

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system, though it is not as comprehensive as the one described in this work.

#### Technical Corrections

The report if Carter (2000) is a major reference and the acknowledgement states that information from that work was downloaded. The reference citation should give the internet address where the report and associated data files can be downloaded (<http://www.cert.ucr.edu/~carter/absts.htm#saprc99> and <http://www.cert.ucr.edu/~carter/SAPRC99.htm>).

Benson (1976) was not on the reference list. They should check and make sure that all the references on the tables are on the list. (I didn't check them all but noticed this omission.)

#### Recommendation

Publish with minor revisions. At least the "technical corrections" need to be made, and a reference to a full report documenting this method (and hopefully also a web address where it can be obtained) needs to be given.

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

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