

Interactive comment on “Assessment of the reduction methods used to develop chemical schemes: building of a new chemical scheme for VOC oxidation suited to three-dimensional multiscale HO_x-NO_x-VOC chemistry simulations” by S. Szopa et al.

S. Szopa et al.

Received and published: 20 May 2005

Reply to Anonymous referee 2

We thank referee 1 for the helpful comments.

1. p759. *The approach does not accommodate cyclic compounds and so aromatics*

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(about 30% of the emissions and a larger fraction of the hydrocarbon reactivity) are dealt with using the Carter method. This is limited and it should be made clear that aromatic chemistry is rather uncertain and not well represented in any explicit mechanism. Such uncertainties are, of course, not revealed in the validation approach used in this paper (comparison of explicit and reduced mechanisms).

Cyclic species are indeed treated in these schemes using the parameterisations of Carter, in which the aliphatic secondary products are then handled by the generator. There are two reasons for this "special" treatment:

- Firstly, the current version of the generator of chemical schemes (explicit as well as reduced) cannot handle cyclic species (see the companion paper, Aumont et al., 2005). The reason for (currently) excluding cyclic species is not scientific, but stems from technical coding issues in generating unique names for all molecules (both initially specified and computer-generated), which for cyclic compounds requires particular attention to avoid duplicities. This coding limitation will be removed in the near future.

- Secondly, the aromatic oxidation mechanisms are far from being established, except the initiation reactions by OH. Consequently, the parameterisations used by modellers are mostly based on smog chamber observations, in which parameterization are introduced to fit the NO_x and O₃ concentration profiles. The methods used by modellers to build the parameterisations are described and discussed in Calvert et al. 2002. The uncertainties related to the SAPRC99 parameterisation are presented in Carter, 2000.

Therefore, the reductions tested in this study only concern the chemistry of the aliphatic secondary VOC arising from cyclic species.

Consequently, in the revised manuscript, p759 l27, "The current version of the automatic generator does not allow the treatment of cyclic species. The initiation reactions of the oxidation for those species were written manually using the schemes developed by Carter (2000). The non-cyclic secondary products from these reactions

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were then treated automatically by the generator." is replaced by "The current version of the automatic generator does not allow the treatment of cyclic species (Aumont et al. 2005). Furthermore, except the initiation reactions by OH, the explicit chemical pathways of aromatic species oxidation are far from being established. Parameterisations in common use by modellers were essentially derived by fitting smog chamber observations of NO_x and O₃ (e.g. Calvert, 2002). The initiation reactions of the oxidation for cyclic species were written manually using the schemes developed by Carter (2000). The non-cyclic secondary products from these reactions were then handled automatically by the generator."

2. p760 line 9. Isomers automatically contain the same numbers of carbon atoms; this statement is tautological (functional group comment should be in). The next two sentences are far from clear. What was done about resonance? The sentence beginning The best compromise... is totally meaningless to me.

(same answer done for question (g) of the reviewer 1.) In the revised manuscript, "Only isomers containing the same number of carbon atoms and bearing the same functional groups were grouped together. Attention was paid on the possible resonance between the functional groups, which implies different chemistry. The best compromise between bias and reduction efficiency was found when the species of third or higher generation of stable products were replaced." is replaced by "Every secondary species produced after three generation of stable products (VOC_{prim} → VOC_{sec} → VOC_{third}) is compared with already treated species. Replacement of a product by another is done if (i) it bears the same number of carbon atoms (ii) it contains the same functional groups and (iii) the respective position of functional groups in the species does not induce a particular reactivity for the molecule or its products. For example, a C=C=C-CO- structure cannot be replaced by a C=C-C-CO- structure, these two isomers having distinct behaviour (electron delocalisation).

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3. *The operator approach needs more explanation, even though this is not original work, it is a key component of the approach. So far as I can see, the approach assumes that, for propane for example, no matter whether the reaction sequence proceeds via reaction with R/HO₂, NO, or NO₃, the carbon framework generates acetone. This allows the competition between the peroxy peroxy and NO_x reactions to be properly accommodated and the appropriate carbon number to be represented, so that the requisite number of NO to NO₂ conversions is eventually generated. This issue is taken up again in the discussion of hydroperoxides (p766/7) but my explicit question is not answered. This is a key issue and deserves more discussion and more explicit scheme writing to demonstrate how appropriate the approach is.*

(same answer done for question (l) of the reviewer 1.) The operator approach is not an original work. A complete description of the method can be found in Carter (1990, 2000), Bey (2001). The description done in this paper aims at giving to the reader already accustomed to this method the tracks to understand what is significantly new in our approach (completely described in Laval-Szopa (2003)).

4. *P769. An important issue in representing hydrocarbons is the number of potential NO to NO₂ conversions that can occur. For alkanes this is equal to the number of C-C + C-H bonds. The approach used in this paper of scaling the surrogate flux by the ratio of carbon atoms in the real and surrogate species provides a good (though not exact) representation of this requirement. This issue might be discussed in a bit more detail.*

The reviewer comment was added in the revised manuscript:

(p769,116): "For alkanes and aromatics, the mass of carbon emitted is conserved Ę" is replaced by "An important issue in representing hydrocarbons is the number of potential NO to NO₂ conversions that can occur. For example for alkanes, this is equal to the number of C-C + C-H bonds (e.g. Jenkin et al., 2002). For alkanes and aromatics, this requirement was taken into account to some extent: the mass of carbon emitted is

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conserved ...".

Reference to Jenkin 2002 was added in the bibliography: "Jenkin et al., Atmospheric Environment, 4725-4734, 2002".

5. Finally, how easy will it be for others to use this approach? It is claimed that it is automatic. Will programmes be made available? How much user interaction is needed in generating the final reduced mechanism?

The reduction of a chemical scheme including more than 350 000 species and 2 millions reactions could neither be handled manually nor envisaged. The reduction using operator species and the replacement of secondary species are treated by the same f77 program tailored to the output files of the explicit generator. The distribution of the 64 primary species into the 17 surrogate primary species is done upstream of the use of the generator and mainly manually, but it is quite easy to be done.

The program will be made available to the scientific community. However, the user interface still need major improvement and a full documentation of these programs is not currently available.

Interactive comment on Atmos. Chem. Phys. Discuss., 5, 755, 2005.

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