**Atmospheric
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Comment

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.

Anonymous Referee #2

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This paper provides an interesting and potentially very powerful technique for reducing large explicit mechanisms for use in CTMs. It is increasingly recognised that this sort of approach is necessary ? it is important to capture the essential chemical details, yet fully explicit models are far too large for global applications. The approaches developed by Carter for SAPRC are extensively used, but this represents a new and very useful

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development; it also comprises a way of using the large, automatically generated explicit mechanisms discussed in the companion paper. The approach could, however, be used for any explicit mechanism. The paper should be published. My comments are aimed at making the approach more easily understood and the approaches used more transparent.

Answers to most of these questions can probably be found in other publications, but they should be made explicitly here also.

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

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.

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 NOx 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.

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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.

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?

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

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