

***Interactive comment on* “Mechanism reduction for the formation of secondary organic aerosol for integration into a 3-dimensional regional Air Quality Model: α -pinene oxidation system” by A. G. Xia et al.**

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General Comments:

This paper describes a process for condensing a near-explicit mechanism for the atmospheric oxidation of pinene, with a focus on its prediction of secondary organic aerosol (SOA) and O₃ formation. The problem of reducing such mechanisms is of general interest in air quality modeling, and modeling of the effect of alpha-pinene on SOA formation is also of interest and relevant to the scope of this journal. Except as noted

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below the paper is clearly written and the conclusions are reasonable. However, the discussion of the methods is unclear in some places, and, more significantly, I think the reduction approach is flawed in several respects. Comments on specific issues are as follows.

Specific Comments:

I do not understand the discussion of the "Principal component analysis" method, particularly with regard to eigenvalues and eigenvectors and how the threshold criteria are applied to them. It is not clear what these mean and how these are derived. Also, how do you apply a scalar threshold quantity to a vector? Perhaps someone with a more mathematical background would understand this and know how to apply this method to their mechanisms, but I suspect that the intersection of the sets of people who develop atmospheric mechanisms and would be interested in learning how to reduce them and the people who understand the discussion in this paper about the use of eigenvalues and eigenvectors in this context is probably pretty small. Perhaps some more formulas giving the how quantities are compared to the thresholds are calculated would allow us to understand at least how to apply this method, if not the mathematical background.

I have problems with the utility and general applicability of the "linear lumping method" as discussed in this paper. Under this method, two model species can be lumped if their ratios do not change throughout the model simulation, regardless of the products they form or their impacts on the system. This may be applicable if the compounds being considered for lumping are limited to products of a single emitted species, (as is the case in this paper) but would not be appropriate if they were emitted themselves or were products of different species that were emitted, unless the compositions of the emissions were always the same. Real world models must cover many emitted VOCs (unlike this mechanism, which only has one) whose ratios may change from time to time. By this definition, one could lump an alkane with an aromatic that happens to have the same OH rate constant, despite their very different impacts on ozone and SOA, and the lumping would look very good as long as the input ratios of each in the

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test simulations were the same.

A more generally useful concept of lumping, which is discussed in the introduction but not applied in this work, is to lump together compounds that have similar reactivities, i.e., react with sufficiently close rates and products with sufficiently similar products that their effects on the quantities of interest (e.g., O₃ or SOA) were sufficiently close. A general approach on how to apply this method is not obvious, and if this paper discussed such an approach it would make a real contribution. Nevertheless, this is the usual method used to reduce most mechanisms used for modeling complex mixtures in real atmospheric scenarios. I would think that significant reductions in this mechanism could have been made with relatively small impacts on the predictions of interest by lumping, for example, many of the different ketone, PAN, hydroperoxide, or acid isomers that are formed in this mechanism. At least this lumping by reactivity would not have the biases introduced by simply removing species, as discussed below.

I do not particularly like reduction methods, such as the DRG or DRGEP methods as discussed in this paper, that simply eliminate species, without replacing them by something to make up for the loss. As noted in the paper, this results in biases in the mechanism's simulations. A reduction approach that causes up to 20% biases in the quantities you are most interested in (e.g., O₃ and total SOA) does not strike me as being acceptable. If on the other hand the "unimportant" species were not simply removed, but replaced by some "major" species that is closest to it in reactivity, then at least you would not be biasing the mechanism, and if done properly the resulting errors may tend to cancel out. The replacing species doesn't have to be very close in reactivity to the species being removed for this approach to be better than simply removing the species, i.e., by replacing it by something that is inert.

There is also a special problem if the species being removed is a radical. In this case, reactions forming it change from being propagation to termination processes, and radicals are not conserved. This has a much greater effect on the overall system than if it were replaced by another radical, and results in consistently negative biases

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in overall reactivity.

Removing reactions may not be as necessarily biased an approach as simply removing species, but as noted in the paper if not done properly this can introduce problems. In some cases it may be appropriate to increase the rate constant for competing reactions or somehow lump it with competing processes rather than just removal.

Because of the biases in the reduced mechanisms developed in this work I don't think they have general utility, and I don't think the method as discussed has general utility when applied to other mechanisms.

Technical Corrections:

In the discussion surrounding Equation (1), they should give slightly more detail about what is meant by "stoichiometric coefficient" for reactants and products. The discussion later around Equation (11) indicates that these are positive if the compound is a product and negative if it is a reactant. Maybe this is obvious to everyone but me but I think this should be stated in the discussion with Equation (1) when the notation is first introduced. (I thought it referred to products only when I first read this section.) Also, unless I am confused it appears that Equation (6) and Equation (10) are inconsistent with regard to the sign of these coefficients. If positive coefficients are used for products shouldn't the "-" in Equation (6) be removed since if a compound is the product in a reaction, wouldn't its rate would make a positive contribution to the rate of change of its concentration?

On page 13326 line 7 they refer to "reduced mechanism from stage 4 #2". But to be consistent with Table 1 shouldn't it be #3?

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