Atmospheric Chemistry and Physics Discussions

Interactive comment on **"Modelling the formation and composition of secondary organic aerosol from α- and β-pinene ozonolysis using MCM v3"** *by* **M. E. Jenkin**

Anonymous Referee #2

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In this study, the author uses the nearly explicit Master Chemical Mechanism v3 to predict the oxidation products for the reactions between the pinene isomers and ozone. An equilibrium partitioning mechanism and an acid chaperone dimer formation mechanism are then used to predict the formation of secondary organic aerosol from these products using the kinetic approach of Kamens. In general, this is a well written, interesting, and timely manuscript, and I recommend its publication. Major points of interest are that hydroperoxides play a major role in secondary organic aerosol formation and that both the use and the choice of a hydroxyl radical scavenger influence the organic aerosol yield by altering the HO2 to RO2 ratio. However, numerous issues must be addressed prior to publication.

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Interactive Discussion

Discussion Paper

Before reactions (R3) and (R4), what is the basis for saying that the major oxidation route of 2-butanol occurs at a percentage of 64?

Reaction (R4) has an error Ű the reactant should be CH3C(OH)C2H5.

In the first reference to Table 1, it is unclear what molecular weight is used to estimate partitioning coefficients. Is it the 130 g/mol referenced later? If so, it should be mentioned here. If not, what molecular weight is used? 130 g/mol seems somewhat low based on previous estimates, and this value should be justified if it is in fact being used.

I do not feel that the discussion of solid vapor pressure adds much to the manuscript, especially since the solid vapor pressures are used at all in the calculations. While many of the species would be present as solids if the aerosol were a single component, it is likely that freezing point depression would lead to the mixture being an amorphous liquid.

The method used to calculate the various kout values and the temperature dependence needs to be justified. The author uses a temperature-dependent method to calculate vapor pressures to determine what species should be included in the partitioning routine. WouldnŠt it then be internally consistent to use Equations (1) and (2) to determine the temperature dependence of partitioning? As it stands now, the author has over 200 fitting parameters that can be varied in order to force the simulation to better fit the experimental results. Would there be any fitting parameters if the authors used Equations (1) and (2)? The only one would most likely be the factor for reduction in vapor pressure when the acid chaperone mechanism is not incorporated. That being said, is it worth presenting the data without the acid chaperone mechanism since our current initial understanding of dimer and oligomer formation indicates that it is extremely important?

In the simulations of the experiments of Yu et al., Table 2 indicates that an unknown RH was used. The author assumes that there is enough water present to scavenge the Criegee radicals. However, the experiments of Yu et al. were performed under

conditions identical to those of previous experiments in the same chamber (Odum et al., Hoffmann et al., and Griffin et al.). The RH for those experiments was approximately 5%. Will incorporation of a RH of 5% affect the results of the authorŠs simulations of the Yu experiments?

In Table 3, observed yields should be included. This would add credence to the authorŠs statement that simulations are in general agreement with experiments.

Why would the acid chaperone mechanism be so highly dependent on temperature, especially compared to the partitioning mechanism that is driven by the highly temperature-dependent vapor pressure?

There are additional experiments provided in Hoffmann et al. and Griffin et al. that would allow for additional comparison of SOA yield, even if speciation of SOA was not available. In the speculative modeling studies, it is always best to simulate as much data as possible.

The temperature sensitivity presented in Figure 9 adds little to the paper as such behavior has been presented previously (Sheehan and Bowman, 2001).

Additional reference (others are already cited in the original paper):

Sheehan, P.E., Bowman, F.M., 2001. Estimated effects of temperature on secondary organic aerosol concentrations. Environmental Science and Technology 35, 1806-1817.

Interactive comment on Atmos. Chem. Phys. Discuss., 4, 2905, 2004.