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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 #3

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General Comments:

This manuscript describes results of modeling studies of secondary organic aerosol (SOA) formation from reactions of a- and b-pinene with O3. These reactions are thought to be significant contributors to global SOA. The model employs a large set of reactions in the Master Chemical Mechanism and a gas-particle partitioning scheme to obtain detailed information on SOA products, yields, and their dependence on the OH radical scavenger. The comparisons with experimental data on SOA yields and species composition are in reasonable agreement, but there are some discrepancies that require adjustments to the model. Importantly, the vapor pressures of the products must be lowered dramatically to obtain agreement, which suggests that condensed-

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phase reactions are significant. These probably involve reactions of hydroperoxides and carbonyls to form peroxyhemiacetals. A useful method is also employed to obtain agreement with experiments at the early stages of growth, suggesting a possible role for acid dimers in SOA formation. The manuscript is well written and sufficiently concise. It presents all the necessary background material and references (see one suggested addition below). I think it is an important and well-done study and is suitable for publication in Atmospheric Chemistry and Physics. I suggest the following comments be addressed.

Specific Comments:

In a recent paper [Keywood, M.D.; Kroll, J.H. ; Varutbangkul, V.; Bahreini, R.; Flagan, R.C.; and Seinfeld, J.H. (2004) Environ. Sci. Technol. 38, 3343-3350], the effect of OH radical scavengers on SOA formation from the reaction of cyclohexene with O3 has been modeled and compared to measured SOA yields. In the model, organic acids were used as a surrogate for SOA. The results support the idea that the OH scavenger affects the [HO2]/[RO2] ratio, which in turn affects the SOA yield. In addition, a change in the [HO2]/[RO2] ratio can have either a positive or negative effect on the SOA yield, depending on the mechanisms by which acyl peroxy radicals are formed. The expectation is that a larger [HO2]/[RO2] ratio increases SOA for endocyclic alkenes like cyclohexene, and decreases SOA for exocyclic alkenes like b-pinene. The model used here is much more detailed than that used by Keywood et al. (2004), and should provide additional insights into this effect. It seems that the mechanism for the a-pinene reaction is sufficiently different from those of both cyclohexene and b-pinene that the Keywood et al. results may not apply to that system. It would be useful to discuss whether the results of the present paper are in agreement with the mechanism proposed by Keywood et al. (2004) for the scavenger effect, and if it is generally valid to use organic acid formation as a surrogate for SOA.

The "chaperone" mechanism employed here to model the initial stages of aerosol growth clearly provides good agreement between the model and the measurements.

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It is not clear to me, however, if this mechanism is physically reasonable. Are the dimers required in order to lower the vapor pressures of the condensing species or to increase the molecular weight, and thereby have each collision add more mass? If the purpose is only to lower the vapor pressure, could this instead be modeled using collision-controlled nucleation theory and growth, which essentially means koff = 0? Also, does the growth rate obtained with this mechanism still depend on the surface area of the growing particles?

One of the primary goals of experimental and modeling studies of SOA formation is to be able to accurately model SOA formation in the atmosphere. I think it would be useful for the author to discuss a few issues related to this goal: How should chamber data be used with atmospheric models? Should the models be developed by comparing results with chamber data and then applied to the atmosphere, or can data, such as aerosol yields, be incorporated directly into atmospheric models? It would appear that the effect of OH radical scavenger on the SOA yield would preclude the possibility of using chamber data directly in atmospheric models, as is commonly done. Is it possible to design experiments, including the OH scavenger, that will mimic atmospheric conditions such as [HO2]/[RO2] ratios? This seems unlikely.

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