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Atmospheric
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Discussions

Interactive comment on "Kinetic modeling of Secondary Organic Aerosol formation: effects of particle- and gas-phase reactions of semivolatile products" *by* A. W. H. Chan et al.

Anonymous Referee #3

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Overview:

This paper investigates the effects of gas-phase and particle reaction kinetics on observed SOA (secondary organic aerosol) yields. The authors present a "Kinetic model" framework that extends the commonly-employed Odum model to include the kinetics of gas-phase oxidation and particle reactions. Different cases within this Kinetic model are highlighted and represented schematically as well as with theoretical SOA growth curves. The authors do a very good job of describing these cases and under what conditions they may be relevant to chamber experiments. Furthermore, they use data from alpha-pinene ozonolysis, isoprene photooxidation and m-xylene photooxidation chamber experiments to illustrate a few of these cases and how the Kinetic model framework can be used to understand the observed growth curves.

The authors are able to draw a few interesting conclusions from this model regarding the interpretation of chamber experiments, including:

1) SOA growth will not be the same for different amounts of hydrocarbon present (HC(0)) if secondary reactions are present in the gas-phase or in the particles (cases (a) and (c)). This is a consequence of the way in which the SOA growth is plotted, namely as a function of Delta_HC (which will require a different amount of time depending on HC(0)). This point is illustrated nicely in Figure 9.

2) The behavior of the SOA growth curve may provide some insight into the relative importance of kinetic processes (i.e. reactions in the gas phase as well as in the particles). The Kinetic model provides a useful framework for trying to understand this.

3) Even though different controlling mechanisms yield different SOA growth curves, the mechanism of SOA formation cannot, in general, be inferred from them. Measurements of both gas-phase and particle chemical composition are required to distinguish between these different mechanisms.

This paper is well written and provides a framework which will be useful for the community in interpreting chamber experiments and extrapolating those results to the atmosphere. It is of appropriate length and scope for this journal.

Specific comments:

1. In discussing the effect that the extent of reaction has (page 7063), the authors advise consuming “as much parent hydrocarbon as possible for the measurement to be atmospherically relevant.” Since this might require a fast rate of oxidation for a given aerosol residence time in the chamber, it is not clear that this would be atmospherically relevant. Please explain this recommendation more clearly in the text. Also, wouldn’t fractional hydrocarbon reacted then be a more useful parameter than the absolute

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amount of hydrocarbon reacted (Delta_HC)?

2. What is meant by “final organic phase volume” (middle of page 7067)? Is this final particle volume?

3. Throughout the paper, the term “kinetic parameters” is used to describe several equilibrium parameters, including alpha_i (the mass-based stoichiometric coefficient of a semivolatile product i) and K_i (the gas-particle partitioning equilibrium constant). The kinetic parameters should be only the ones that represent the rates of reactions or processes, e.g. k_g, k_p or beta_g, beta_p.

Technical comments:

1. Typo at bottom of page 7062. Remove “is also higher at any given time.”

Interactive comment on Atmos. Chem. Phys. Discuss., 7, 7051, 2007.