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Atmospheric
Chemistry
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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.

A. W. H. Chan et al.

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We would like to thank the referees for the comments. Changes have been made to the manuscript to address these issues. In particular, a section has been added to evaluate the uncertainties of the fitted parameters in the models.

Responses to comments by referee #1:

‘...the comments that "higher HC(0) leads to higher A2" seems to only apply when beta_g = 1. When beta_g $>$ 1, the reverse is true, which is the case in Figure 13. This needs clarification.’

This was a typo. LOWER HC(0) leads to higher A2 at any given deltaHC. This is a

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consequence of plotting deltaMo as a function of deltaHC (and not of time). Since it takes a longer time for a lower HC(0) to achieve the same deltaHC, this allows more A1 to react and convert to A2. This effect is present regardless of the value of betag. It only determines the degree of divergence in growth curves.

'...instead of "consuming as much parent hydrocarbon as possible", the author likely meant "consuming the parent hydrocarbon to the fullest extent" or "consuming all of the parent hydrocarbon"'

The sentence has been corrected as noted.

Responses to comments by referee #2:

'The authors seem to be proposing such empirical models for the several reaction systems in Figure 11-13. However, in the concluding section, the authors pointed out that "it is not generally possible to infer the precise mechanism of SOA formation solely on the basis of SOA growth data." To gauge the utility of the model, therefore, it may be useful to explore the uncertainties of the fitted parameters and whether different variations of the model can perform equally well given the parametric uncertainties.'

The intention of this work was to explore the implications of including kinetic mechanisms of SOA formation in atmospheric models, as applied to different reaction systems, such as the ones in Fig. 11-13. To assess the usefulness of this approach, the growth curves were fitted to the different models and the parameters were obtained via optimization. The recovered parameters were not unique, because the measured SOA growth represents the sum of all aerosol-phase species, while SOA growth described by these models can result from either a first-generation product or a product from further reaction. If gas-phase measurements of the semivolatile compounds are available, the parameters can be decoupled. A section has been added to the manuscript to illustrate this point (section 5.1).

'The use of the term "pseudo first order" in the text and appendix is unorthodox and confusing for students trained in kinetics. Chemical engineers typically refer to reaction kinetics of A+B as pseudo first order when one of the reactants is in excess and the rate (k[A][B] can be written as k'[B] because the change in [A] is negligible. In this case, the kinetics of a second order reaction is written as the product of k'[A], and the mole fraction of A. Even though k' has the units of inverse time, the rate should still depend (implicitly) on the squared concentration of A. Is an assumption being made that the mole fraction is roughly constant? If so, please state and justify.'

The mole fraction is not assumed to be roughly constant. The kinetics of the reaction is still second-order: the rate is not only proportional to [A], but also on the organic phase concentration of species A. The rate constant still has the units of inverse time and we can still take the ratio of the bimolecular reaction rate constant to that of hydrocarbon oxidation as a dimensionless parameter. To avoid confusion, the rate constant is no longer referred to as "pseudo-first-order", but rather it has the dimensions of inverse time only (first paragraph of section 4.1 and last paragraph of Appendix).

Responses to comments by referee #3:

'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 amount of hydrocarbon reacted (Delta_HC)?'

Based on the model observation that the extent of reaction also affects the SOA yield measured in a chamber experiment, we recommend that measurements of SOA yield be made when the extent of reaction is atmospherically relevant. Using very high HC(0) might not be desirable when there are multiple reactions. If wall loss of semivolatile compounds is the dominant process, faster oxidation is better. Otherwise, there is clearly a tradeoff between using a fast rate of oxidation to consume most of the parent HC, and using a slower (but closer to ambient) rate of oxidation and reacting less HC.

We have considered using a dimensionless quantity for the x-axis (such as the fractional hydrocarbon reacted), but we would also have to use a dimensionless quantity on the y-axis, such that chamber results can be compared and the parameters can be extrapolated to describe SOA growth in the atmosphere. We have considered using fractional growth (delMo/delMo_final), but delMo_final is not linear in HC0 due to semivolatile partitioning.

‘What is meant by "final organic phase volume" (middle of page 7067)? Is this final particle volume?’

This is the final particle volume in the organic phase. We assume that the inorganic phase is not involved with gas-particle partitioning of organic species, which occurs immediately once the gas-phase concentration reaches saturation.

‘Throughout the paper, the term "kinetic parameters" is used to describe several equilibrium parameters, including alpha_i (the mass-based stoichiometric coeffficent 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.’

This has been corrected. "Kinetic parameters" now only refer to rate constants or ratio of rate constants. alpha_i and K_i are now referred to as "equilibrium parameters". (Section 3.5 and captions of Fig. 13)

‘Typo at bottom of page 7062. Remove "is also higher at any given time."’

The sentence has been corrected as noted.

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