

## ***Interactive comment on “Nanoparticle Growth by Particle Phase Chemistry” by Michael J. Apsokardu and Murray V. Johnston***

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The authors thank the referee for significant and quite helpful comments. We have made several changes to the manuscript to address this referee's concerns.

Referee comment #1:

I guess my first reaction upon reading this paper is one of déjà vu. The authors devote no text to describing the rich history of modeling the growth of particles from a few nanometers to CCN-relevant sizes, but in fact there have been several papers devoted to this. The one that is most similar to the current manuscript is a paper by Vestervinen et al., entitled “Effect of particle phase oligomer formation on aerosol growth” (<https://doi.org/10.1016/j.atmosenv.2006.10.024>). From what I can tell – and admit-

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tedly I didn't spend nearly as much time reading this paper as the authors should – the model described in that 2007 paper does an excellent job with the organics and particle-phase reactions, with the added benefits that the study by Vesterinen et al. (a) provides a sensitivity study of the effect of the dimer formation rate constant; (b) compares modeling results to chamber studies; (c) includes the rate of monomer formation and, I think, includes the possibility that SVOC may evaporate; and (d) provides a hypothesis for uptake that involves the formation of an organic liquid layer onto an ammonium sulfate seed. The main difference between the two studies is that the current one includes the uptake of ammonia and sulfuric acid, whereas the earlier one assumes an ammonium sulfate seed particle. Here is an opportunity for the authors to distinguish themselves from this earlier work, but in doing so they need to acknowledge the prior work and provide an explanation for why this builds upon existing models and how their results compare. There are likely other attempts at modeling growth to CCN size, but the reader would not get a sense that anything has been done in this area considering the scarcity of discussion of prior work by the authors.

#### Author response #1:

Thank you very much for this comment. We are aware of the Vesterinen paper and are cited in some of our previous papers as well as other modeling work related to oligomers. We have addressed this comment in several ways.

First, we have added the following paragraph to section 1 lines 70-79 to briefly review modeling of oligomers in secondary aerosol formation, citing a total of 6 new publications and a seventh one that was already cited elsewhere in the manuscript.

“The role of particle phase oligomerization in SOA formation has been the focus of several modeling studies. Owing to the high molecular weight and corresponding low volatility of oligomer products (Shiraiwa et al., 2014), early work assumed an irreversible process (Vesterinen et al., 2007), which proved effective for predicting the yields of freshly formed aerosol in chamber experiments and estimating the magnitude

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of the oligomerization rate constant needed for the process to impact yields. More recent models have included reversibility (Roldin et al., 2014; Trump and Donahue, 2014), which is needed to reproduce perturbations of freshly formed SOA such as changes induced by isothermal dilution, thermal degradation and/or aging. Regional air quality models show that oligomerization has the potential to significantly increase the SOA mass concentration (Aksoyoglu et al., 2011; Lemaire et al., 2016), and accurately representing this chemistry in these models is perhaps the greatest uncertainty for predicting SOA formation (Shrivastava et al., 2016).”

Second, we made additions to the manuscript in several places to indicate the “value added” aspect of our study relative to the body of work summarized in the new paragraph above. These include:

(1) Our manuscript explicitly discusses particle size effects in the sub-100 nm diameter regime. To address this point, we made the following addition to section 1 lines 80-85: “The influence of particle size, or more precisely the relative roles of particle volume and surface area, on oligomer formation in SOA has received relatively little attention though these effects are implicit in all of the models. Particle size has been discussed primarily in the context of accumulation mode particles greater than 100 nm in diameter (Roldin et al., 2014; Shiraiwa et al., 2013; Vesterinen et al., 2007). The Vesterinen study did report aerosol yield functions from simulations starting with 20 nm diameter seed particles, and the results suggested that particle phase chemistry could enhance growth rates under atmospherically relevant conditions.”

(2) Our modeling parameters more closely resemble those in a flow reactor than a batch reactor, which was the main focus of other modeling studies of laboratory data. This becomes important when we discuss modeling of recent experiments performed in a flow tube (see response to comment 2 of referee #1).

We made the following addition to final paragraph of section 1 lines 95-99: “The modeling approach is similar to that used in previous studies, though the reaction condi-

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tions studied here more closely resemble those of an “open” laboratory reactor where aerosol flows into and out of the reactor (i.e. flow reactor), as opposed to a “closed” batch reactor which was the main focus of previous modeling work. The results are discussed in the context of recent size-resolved molecular composition measurements (performed with flow reactors) and the potential atmospheric impact of particle phase chemistry.”

We also made the following addition to end of first paragraph of section 2 lines 110-112: “The gas phase mixing ratios are assumed to be constant over time (steady state) as might be achieved in a flow reactor, and the values chosen are typical of what might be observed during NPF in a boreal forest (Vestenius et al., 2014). ”

(3) Our manuscript presents a detailed discussion of particle size-dependent molecular composition, including a discussion of recent experimental results (see response to comment 2 of referee #1). While particle composition is an implicit aspect of previous studies, it has not been explicitly discussed in detail. For example, plots similar to Figures 3 and 4 simply do not exist in the literature nor have they been discussed in that manner. To address this topic, we revised the first paragraph of section 3.4 lines 306-320 as follows:

“For the modeling conditions studied here, particle phase chemistry influences both the molecular composition and growth rate of sub-100 nm diameter particles under atmospherically relevant conditions, provided that the rate constant is above about  $10^{-3}$  M $^{-1}$ s $^{-1}$  for semi-volatile reactants having a saturation concentration on the order of 1  $\mu$ g/m $^3$  and gas phase mixing ratios on the low pptv level. Based on the condensed phase concentration dependence of reactants on the reaction rate, a rate constant on the order of  $10^{-1}$  M $^{-1}$ s $^{-1}$  would be required for semi-volatile reactants having saturation concentrations on the order of 10  $\mu$ g/m $^3$ . These rate constants (Ziemann and Atkinson, 2012) and saturation concentrations (Trump and Donahue, 2014) are in the range of those expected for e.g. monoterpene accretion chemistry. The overall conclusion that accretion chemistry may contribute to nanoparticle growth and/or composition

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under atmospherically relevant conditions is similar to that reached by (Vesterinen et al., 2007). The current work provides an additional, fundamental basis for interpreting recent experimental measurements of molecular composition as a function of particle size in the case of monodisperse aerosols (Tu and Johnston, 2017), or more generally, volume-to-surface area ratio for polydisperse aerosols (Wu and Johnston, 2017). In each study, the relative concentration of accretion products increased approximately linearly with particle size (or volume-to-surface area ratio) as predicted by Figure 4b. Below, we estimate the magnitudes of the reaction rate constants needed to reproduce the experimental results.”

(4) To further drive home the emphasis on size-dependent particle composition, we have added a new figure and text showing how the identities of the monomer reactants affect particle composition and growth. To the authors’ knowledge, there are no other reports in the literature modeling the relative roles of SVOC and NVOC in accretion chemistry; most simply discuss accretion chemistry in terms of SVOC alone. Accordingly we have revised the last two paragraphs in section 3.3 lines 285-304 and added a new Figure 5b:

“Accretion chemistry is not necessarily restricted to SVOC molecules. If two NVOC molecules react in the particle phase to form DIMER, then the diameter growth rate will not change with increasing particle diameter since NVOC uptake remains unaffected, though the molecular composition will change with increasing diameter. A calculation demonstrating this principle is shown in Figure S3 (growth rate vs. particle diameter) and Figure S4 (DIMER/NVOC mass ratio vs. particle diameter). If one SVOC molecule reacts with one NVOC molecule to form DIMER, both the growth rate and molecular composition change with increasing particle diameter. A calculation demonstrating this principle is shown in Figure 5b, where growth rate vs. particle diameter is compared for SVOC-SVOC, NVOC-NVOC and SVOC-NVOC dimer formation reactions. The SVOC-NVOC reaction enhances the particle growth rate at a much smaller particle diameter than the SVOC-SVOC reaction. This enhancement arises from KEMPD of

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SVOC, which favors formation of the SVOC-NVOC dimer over the SVOC-SVOC dimer at small particle sizes. Because of the greater potential of the SVOC-SVOC reaction to transform semi-volatile matter into non-volatile matter, its contribution to growth rate eventually overcomes that of the SVOC-NVOC reaction as the particle size increases.

Taken together, Figures S2-S4 show that the observation of a change in DIMER to monomer ratio with increasing particle diameter does not necessarily indicate an enhancement of the particle growth rate by accretion chemistry. On the other hand, Figure 5b shows that the lack of a particle size-dependent change in the growth rate does not necessarily mean that particle growth rate is unaffected by accretion chemistry. Nonetheless, these results illustrate how experimental measurements of particle size-dependent changes in molecular composition and growth rate can supplement traditional measures, such as aerosol yield and perturbations due to e.g. isothermal dilution, to better constrain SOA formation models with regard to particle phase chemistry.”

(5) Finally, we added the following text to the end of Section 3.3 lines 365-371 that succinctly summarizes the most important “value added” aspect of the work we report here: “The work presented here suggests that experimental measurements of molecular composition as a function of particle size and/or aerosol volume-to-surface area ratio can supplement traditional measurements (aerosol mass yields, perturbations caused by isothermal dilution, etc.) for constraining aerosol formation models. Future modeling of size-dependent molecular composition should include physico-chemical parameters such as diffusion, phase separation, reaction reversibility, etc. (Liu et al., 2014; Mai et al., 2015; Riipinen et al., 2012; Shiraiwa et al., 2012; Song et al., 2015; Trump and Donahue, 2014; Zaveri et al., 2014) that may influence the contribution of particle phase chemistry to nanoparticle growth.”

Referee comment #2.

In addition, the authors provide a fairly terse interpretation of the modeling results

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and no quantitative comparisons of their results to observations. In my view this is a major weakness of the manuscript. The system under study – ultrafine aerosol particle growth from terpene oxidation and on ammonium sulfate seed particles, is one of the most widely studied chemical systems, both in lab and in the field. The fact that no data are directly compared to modeling results is, in my view, a missed opportunity that does nothing to validate the assumptions that went into the development of the model. In summary, this manuscript should acknowledge prior studies and discuss how their results both compare to and improve upon understanding of those earlier models. In addition, some comparison of lab or field data seems like a reasonable thing to do for any new model presented to the community. At the very least, the authors could perform a calculation similar to that of Vestner et al. and turn off ammonia and sulfuric acid and study organic uptake and particle-phase reaction chemistry onto ammonium sulfate seed particles.

Author response #2.

To address this comment, we renamed Section 3.4 “Comparison to Recent Experimental Measurements and Atmospheric Implications”, and we added three new paragraphs in lines 306-355 to describe the use of the model to provide semi-quantitative insight into the experimental results of Wu and Johnston (2017) and Tu and Johnston (2017). Specifically, in the revised manuscript we estimate numerical values for dimerization rate constants that explain the experimental results along with their atmospheric relevance. Here are the paragraphs added:

“For the modeling conditions studied here, particle phase chemistry influences both the molecular composition and growth rate of sub-100 nm diameter particles under atmospherically relevant conditions, provided that the rate constant is above about  $10^{-3} \text{ M}^{-1}\text{s}^{-1}$  for semi-volatile reactants having a saturation concentration on the order of  $1 \mu\text{g}/\text{m}^3$  and gas phase mixing ratios on the low pptv level. Based on the condensed phase concentration dependence of reactants on the reaction rate, a rate constant on the order of  $10^{-1} \text{ M}^{-1}\text{s}^{-1}$  would be required for semi-volatile reactants having satura-

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tion concentrations on the order of  $10 \mu\text{g}/\text{m}^3$ . These rate constants (Ziemann and Atkinson, 2012) and saturation concentrations (Trump and Donahue, 2014) are in the range of those expected for e.g. monoterpene accretion chemistry. The overall conclusion that accretion chemistry may contribute to nanoparticle growth and/or composition under atmospherically relevant conditions is similar to that reached by (Vesterinen et al., 2007). The current work provides an additional, fundamental basis for interpreting recent experimental measurements of molecular composition as a function of particle size in the case of monodisperse aerosols (Tu and Johnston, 2017), or more generally, volume-to-surface area ratio for polydisperse aerosols (Wu and Johnston, 2017). In each study, the relative concentration of accretion products increased approximately linearly with particle size (or volume-to-surface area ratio) as predicted by Figure 4b. Below, we estimate the magnitudes of the reaction rate constants needed to reproduce the experimental results.

In the Wu study (Wu and Johnston, 2017), decamethylcyclopentasiloxane (D5) reacted with OH in the gas phase to produce secondary aerosol having three types of products: ring-opened species, oxidized monomers containing OH and/or CH<sub>2</sub>OH functionalities in place of CH<sub>3</sub>, and dimers of D5 and/or its monomer oxidation products. The dimer concentration in the particle phase (as indicated by the signal intensities of corresponding ions produced by electrospray ionization) increased linearly with increasing volume-to-surface area ratio of the aerosol relative to the (non-volatile) ring-opened products. This dependence suggested that ring-opened products were formed in the gas phase and subsequently condensed onto the particles, while dimers were produced directly in the particle phase from monomers. Monomer gas phase mixing ratios in these experiments were on the order of a few ppbv, which is similar in magnitude to the levels measured in a university lecture hall (Tang et al., 2015). Using these values in conjunction with the basic model described above, we estimate the dimerization rate constant had to be in the  $10^{-3}$  to  $10^{-1} \text{ M}^{-1}\text{s}^{-1}$  range to achieve the level of dimerization observed, given that most of the monomers expected to participate in the reaction had estimated saturation concentrations in the  $10^2$  to  $10^3 \mu\text{g}/\text{m}^3$  range. Smaller rate con-

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stants would have been unable to produce a sufficient amount of dimers, while higher rate constants would not have shown a volume-to-surface area ratio dependence of the dimer concentration since the reaction rate would have been limited by transport of reacting monomer to the particle surface.

In the Tu study (Tu and Johnston, 2017),  $\beta$ -pinene ozonolysis produced SOA having systematic changes in molecular composition as a function of particle size. The relative concentrations (as indicated by the signal intensities of ions produced by electrospray ionization) of higher order oligomers, i.e. trimers and tetramers, increased linearly with increasing particle size, similar to Figure 4b. The total oligomer signal intensity was comparable to our previous study of  $\alpha$ -pinene SOA formed under similar reaction conditions, where the oligomer content was experimentally determined to be about 50% of the total SOA mass (Hall IV and Johnston, 2011). For the Tu study, we estimate the NVOC mixing ratio to be approximately 2 ppbv based on the yield estimate of Ehn et al. (Ehn et al., 2014) for  $\beta$ -pinene ozonolysis. We estimate the mixing ratios for the 10  $\mu\text{g}/\text{m}^3$  and 100  $\mu\text{g}/\text{m}^3$  saturation concentration bins to be approximately 30 ppbv and 40 ppbv, respectively, based on the volatility basis set (VBS) parameterization of Donohue and coworkers for  $\alpha$ -pinene ozonolysis (Donahue et al., 2012; Trump and Donahue, 2014). For these conditions, condensational growth and/or partitioning of molecular species alone are able to explain the overall growth of particles to about 80-100 nm in diameter during the  $\sim 20$  s residence time of the flow reactor, though the modeling results are extremely sensitive to the mixing ratios and VBS parameterization used. However, condensational growth and partitioning cannot explain the high abundance of accretion reaction products that were measured. We estimate that the reaction rate constants needed to form dimers and higher order oligomers in sufficient amounts had to be at least on the order of  $10^{-3} \text{ M}^{-1}\text{s}^{-1}$ . (The required rate constant is dependent on SVOC volatility, with a larger rate constant needed for saturation concentrations above 10  $\mu\text{g}/\text{m}^3$ .) Together, the modeling work performed here and the experimental measurements in the Wu and Tu studies all suggest that reaction rate constants on the order of  $10^{-3}$  to  $10^{-1} \text{ M}^{-1}\text{s}^{-1}$  are needed for accretion chemistry to be

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relevant to SOA molecular composition and growth.”

With regard to the reviewer suggestion to perform a calculation similar to Vesterinen (2007), we decided instead to add the following sentence to lines 280-283 of section 3.3, which directly compares an aspect of our results in Figure 5 (the 10-1 M-1s-1 calculation in this figure) to the Vesterinen work: “The lack of a particle size dependence on SOA growth in the limit of a fast reaction rate has also been suggested in a modeling study of SOA produced by  $\alpha$ -pinene ozonolysis (Gatzsche et al., 2017). It is also consistent with the work of Vesterinen et al. (Vesterinen et al., 2007) who showed a linear increase of particle diameter with time when the reaction rate constant was sufficiently large.”

We also added the following to section 3.3 lines 313-315: “The overall conclusion that accretion chemistry may contribute to nanoparticle growth and/or composition under atmospherically relevant conditions is similar to that reached by (Vesterinen et al., 2007).”

Additional Author response to comments 1 and 2 of referee #1:

The abstract has been revised (lines 6-20) to reflect changes to the manuscript discussed above. Here is the revision:

“The ability of particle phase chemistry to alter the molecular composition and enhance the growth rate of nanoparticles in the 2-100 nm diameter range is investigated through the use of a growth model. The molecular components included are sulfuric acid, ammonia, water, a non-volatile organic compound, and a semi-volatile organic compound. Molecular composition and growth rate are compared for particles that grow by partitioning alone vs. those that grow by a combination of partitioning and an accretion reaction in the particle phase between two organic molecules. Particle phase chemistry causes a change in molecular composition that is particle diameter dependent, and when the reaction involves semi-volatile molecules, the particles grow faster than by partitioning alone. These effects are most pronounced for particles larger than about

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20 nm in diameter. The modeling results provide a fundamental basis for understanding recent experimental measurements of the molecular composition of secondary organic aerosol showing that accretion reaction product formation increases linearly with increasing aerosol volume-to-surface area. They also allow initial estimates of the reaction rate constants for these systems. For secondary aerosol produced by either OH oxidation of the cyclic dimethylsiloxane (D5) or ozonolysis of  $\beta$ -pinene, oligomerization rate constants on the order of  $10^{-3}$  to  $10^{-1}$  M $^{-1}$ s $^{-1}$  are needed to explain the experimental results. These values are consistent with previously measured rate constants for reactions of hydroperoxides and/or peroxyacids in the condensed phase.”

Referee comment #3: (minor points)

Title: Since the size range covered here is sub-100 nm diameters, then it would seem natural to use the accepted term “ultrafine aerosol particle” rather than “nanoparticle.” The authors cite their own studies often exclusively when several other seminal studies have contributed significantly to developing current understanding. Examples include “Nanoparticle composition and growth rate are dominated by organic matter,” and the “growth rate of nanoparticles by sulfuric acid and base is predicted by condensational growth model,” both of which had a history of important breakthroughs prior to the work of Bzdek and Pennington (here are just a few): Nanoparticle growth from sulfuric acid and ammonia: <http://onlinelibrary.wiley.com/doi/10.1029/2005JD005935/abstract> Nanoparticle growth from sulfuric acid and organics: <http://onlinelibrary.wiley.com/doi/10.1029/2005GL023827/pdf> Nanoparticle growth from organics: <http://onlinelibrary.wiley.com/doi/10.1029/2007GL032523>.

Author response #3:

Title: We have also gone back and forth on the use of “ultrafine” vs. “nanoparticle” in the title. We have stuck with “nanoparticle” because we consider the full size range down to 2 nm, and in much of the scientific literature, the nomenclature is such that “nanoparticle” is used for the entire size range below 100 nm.

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Citations: We have trimmed back the Bzdek/Pennington citations and added others. Specifically, paragraph 2 of section 1 lines 36-45 has been modified in the following way:

“The three main chemical species that contribute to ambient nanoparticle growth are sulfuric acid, a neutralizing base typically ammonia, and organic matter. The growth rate due to sulfuric acid along with neutralizing base is accurately predicted by experimental measurements of gas phase mixing ratio and particle phase composition using a condensational growth model (Bzdek et al., 2013; Pennington et al., 2013; Smith et al., 2008; Stolzenburg et al., 2005), though sulfuric acid represents only a minor fraction of the total growth rate of ambient particles (Kuang et al., 2010, 2012; Weber et al., 1996; Wehner et al., 2005). Nanoparticle composition and growth rate are dominated by organic matter (Bzdek et al., 2011, 2012, 2013, 2014a, 2014b; Pennington et al., 2013; Riipinen et al., 2012; Smith et al., 2008), and though significant molecular insight has been gained (Bianchi et al., 2016; Ehn et al., 2014; Kulmala et al., 2013; Riccobono et al., 2014), current growth models for organic matter appear to be incomplete (Hallquist et al., 2009; Tröstl et al., 2016).”

We have also modified references elsewhere in the manuscript (paragraph 3 of section 1; paragraph 1 of section 2) to emphasize more broadly the contributions of others.

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