

***Interactive comment on “Alkene ozonolysis SOA:
inferences of composition and droplet growth
kinetics from Köhler theory analysis” by
A. Asa-Awuku et al.***

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We would like to thank the referee for the thorough comments; our responses follow.

General comments

This manuscript addresses the properties of secondary organic aerosol formed in the oxidation of three alkenes: terpinolene, 1-methyl cycloheptene and cycloheptene. The authors aim at determining ccn properties, surfactant characteristics and droplet growth kinetics. The authors should be complemented for presenting new ideas to elucidate the cloud droplet activation of SOA. In this work they suggest to add salt to extracts of filter samples of organic aerosols and determine critical supersaturations of particles generated from these mixtures. From the measured activation curves the authors

infer surface tensions at the point of activation as well as organic molecular weights. The manuscript in its current state does however not provide enough consideration on the experiments and related uncertainties nor on the underlying assumptions and theory used to model the data and infer surface tensions and molecular weights. The magnitude of uncertainties introduced by various assumptions: densities, van't Hoff factors and mass fractions of organic and inorganic material in the particles should be addressed.

We thank the reviewer for the encouraging thoughts. We have reprocessed the data, in lieu of work published since this manuscript is submitted and have assessed the uncertainty in molar volume to van't Hoff factor, and mass fraction of organics. The molecular weight sensitivity to density is also assessed.

Specific comments

There is too little information about the conditions in the smog chamber. What was the Reactant concentrations? what was the time scale? Relative humidity and temperature? In the study by Gao et al. 2004a seed particles and an OH scavenger were used – were seed particles and OH scavenger also used in the present study?

The text has been rewritten as follows: “Secondary organic aerosol is generated from the seedless dark ozonolysis of three parent alkenes (cycloheptene, 1-methyl cycloheptene and terpinolene) and collected upon Teflon filters. The ozonolysis experiments were performed in the Caltech dual 28 m³ Teflon chambers under dry conditions (> 5% relative humidity), a detailed description of which can be found in Keywood et al. (2004). The ozone mixing ratio was three times that of the reactant concentration (Table 1) to insure adequate oxidation (Gao et al., 2004a).”

Page 8987: Likewise, in relation to the CCN experiments more information on the experimental details would be useful. The authors should show examples of activation curves to give an impression of the quality of the data. How was doubly charged particles accounted for in the analysis? I have some questions regarding the calculated

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mass fraction of inorganic material: 1) The organic carbon-to-carbon ratio seems to be a quite uncertain parameter. It should be better explained what this ratio is and how it was obtained. How is a general factor of 2 justified from the rather limited information in Table 1?

Additional details to the experimental CCN activity have been added. Doubly charged particles were neglected during the fitting of the aerosol to the sigmoidal CCN/CN curve. This can be safely done, given that the peak in the dry aerosol size distribution generated in the atomizer for CCN measurements is much less than 80nm, and doubly-charged particles are not a substantial fraction of the CCN data. We have included examples of the activation curves in the revised manuscript. Each experiment is repeated a minimum of four times, the variability of which is expressed in the error bars in Figure 1-3. We have also included a detailed description of the experimental procedure and setup.

The organic carbon to carbon ratio is estimated in our work from the speciation information available from Gao et al, 2004a and the supplemental data associated with that work. Knowing the molecular formulae of the speciated compounds, and their percentage abundance, we can calculate the mass of carbon to the mass of the compound. All this information is available from Gao et al., 2004. This point has been clarified in the text.

2) Evaporation: Glutaric acid is listed as a major soluble organic compound - it has a high vapor pressure. What is the time that the particles spend between the atomizer and the ccn-counter? Could evaporation of the organic fraction of the atomized aerosol particles take place and thus change the composition of the particles studied compared to the composition of the mixture in the atomizer?

Evaporation of the organic fraction of the atomized aerosol is always a possibility with organic aerosol (Asa-Awuku et al., 2009). To explore volatility effects, CCN activation experiments were carried out at double temperature gradient (but same supersatu-

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ration); the CCN activity of the aerosol remained the same, suggesting that volatility effects may not be as important.

Page 8988: The authors mention critical micelles: this should be more thoroughly addressed can the relevant range of the critical micelle concentrations for the major products be estimated? When are micelles formed in the present study?

This discussion was removed, as the amount of SOA mass available in filter samples is insufficient to approach a critical micelle concentration.

Page 8989. It says that "If the salt mass fraction exceeds 50% the majority of dissolved solute is usually from the inorganic salt", I suggest to give some actual calculated values from the current study as example. Why was 33% (and not > 50%) used in many of the experiments? Which van't Hoff factor was used for ammonium sulfate?

Unfortunately, there was not enough sample to investigate the sensitivity to all salt fractions. We carried out some experiments with 33% ammonium sulfate to ensure that the contribution of organic to total hygroscopicity was present, but minor. We assume an ammonium sulfate van't Hoff factor = 2.5 (Rose et al., 2008). Subsequent estimations with a comprehensive thermodynamic theory (Bougiatioti et al., 2009) exhibited minimal impact on our results.

Page 8990 If the organic contribution to the Raoult effect is not negligible the authors say that it must be accounted for in equations 6-8. To help the reader it should be better explained how this is actually done.

These issues are now thoroughly discussed in Moore et al., (2008), and is now cited in the manuscript.

The authors do not address partitioning of surfactants between the bulk and the surface as discussed by Sorjamaa et al. [1-3] and Li et al. [4]. Surfactant partitioning is not accounted for in the traditional derivation of the critical supersaturation (power dependence of $3/2$) used by the authors - it is not clear how it looks if surfactant partitioning

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is included in the derivation of the critical supersaturation.

This is true. Moore et al. (2008) saw these effects quite strongly, especially for the high critical supersaturation particles; although the partitioning theory of Li et al., 1998; Sorjamaa and Laaksonen, 2006; Sorjamaa et al., 2004 are not considered, one can, by combining measurements of “pure” and “salted” CCN samples, deconvolute the surface tension and solute contributions to aerosol hygroscopicity (Moore et al., 2008; Asa-Awuku et al., 2009; Englehart et al., 2008). We do not expect a more detailed level of theory available any time soon (including that of partitioning) because of the highly complex nature of the soluble organic.

Page 8991. What were the estimated values of surface tension used to obtain the INCA parameter? Method b1 in Padro et al. assumes that there are no strong surfactants present at the point of activation, yet the conclusion is that surface active compounds do exist in the mixture. This does not seem consistent?

The INCA (now FCA) parameter is independently determined from fits of CCN activity measurements. Using method b1 is consistent, as long as low critical supersaturation data is used (because such activated CCN are dilute at the critical wet diameter, and surface tension depression is minimal).

Page 8992. Figures 1-3: it should be explained what the solid lines in the figures are. How can compounds that are not surfactants based on the $m-1/2$ dependence? The $m-1/2$ dependence should be demonstrated more clearly, for example in a table.

Done. We have revised the discussion accordingly.

Page 8993+8994 The density of 1.4 was adopted by Goa et al. from Kalberer et al. [5]. Also it is discussed by Gao et al. 2004 [6] that the density could very well be larger than 1.4 and that the density is a quite uncertain parameter. What are the consequences of a different density?

Molar Volume is insensitive to density uncertainties, but molecular weight is. The sen-

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sitivity analysis now addresses these issues.

Table 5 and related text: The inferred surface tension shows roughly 15% depression from pure water, only in the case of cycloheptene and terpinolene SOA with 33% ammonium sulfate. It does not seem justifiable to make conclusions and comparison with HULIS based on this without consideration of the uncertainties (in particular for terpinolene), assumptions and the lack of information about terpinolene SOA (Table 1).

Indeed. This is now revised accordingly.

How much should the van't Hoff factor used for the organics (cycloheptene as well as terpinolene) deviate from one, or how much should the experimental value be in error to get an inferred surface tension equal to that of water or on the other extreme HULIS (e.g. Kiss et al.)? I miss numerical values on critical supersaturations to compare different approaches. For example calculated values of critical supersaturations and inferred surface tensions using different values of the parameters (van't Hoff factor, density, m_i) could be given in a table together with experimental values including uncertainty ranges.

According to Dinar et al. (2006), the van't Hoff factor uncertainty can be up to 20%. The water-soluble fraction of the SOA examined here may disassociate to a lesser extent, so that the values calculated are more likely to be an overestimation of the actual error.

The authors state that the agreement of the effective molecular weights with the Gao data [6] validates the use of inferred surface tension values in KTA - this seems like an overstatement since the inferred values on $m_{inorganic}$ relies on results from Gao et al [6]?

The only information used from Gao et al. 2004a is the C/OC ratio. All other measurements are independent.

Technical Comments:

The notation is not consistent: Page 8988 $m_{inorganic}$, page 8990 m_i Explain what the
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difference between m_i and m_o is. In the text the term m_{organic} is used

Done.

Reference to Gao et al. 2004a: Volume number (108) is missing

Reference corrected.

References:

We have added references where appropriate.

References Asa-Awuku, A., Engelhart, G.J., Lee, B.H., Pandis, S.N., and Nenes, A. (2009) Relating CCN activity, volatility, and droplet growth kinetics of beta-caryophyllene secondary organic aerosol, *Atmos. Chem. Phys.*, **9**, 795–812

Engelhart, G.J., Asa-Awuku, A., Nenes, A., and Pandis, S.N. (2008) CCN activity and droplet growth kinetics of fresh and aged monoterpene secondary organic aerosol, *Atmos. Chem. Phys.*, **8**, 3937-3949

Moore, R.H, Ingall, E.D., Sorooshian, A., and Nenes, A. (2008) Molar Mass, Surface Tension, and Droplet Growth Kinetics of Marine Organics from Measurements of CCN Activity, *Geoph.Res.Let.*, **35**, doi:10.1029/2008GL033350

Padró, L.T., Asa-Awuku, A., Morrison, R., and A. Nenes (2007) Inferring thermodynamic properties from CCN activation experiments: single-component and binary aerosols, *Atmos. Chem. Phys.*, **7**, 5263-5274

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