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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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The authors present measurements of CCN activity for aerosol generated from ozonolysis of three alkene hydrocarbons. In addition surface tension measurements for dilute solutions are presented. The data are analyzed using Kohler Theory Analysis (KTA) which attempts to infer effective molecular weight and solution surface tension during cloud droplet activation from the CCN measurements.

The data are novel and relevant to the ACP audience. However, the experimental description is not very detailed and technical aspects of the work should be explained more thoroughly in a revised manuscript. Most importantly however, I have reservations about the interpretation of the data and cannot agree with the conclusions drawn.

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Specifically, the use of critical supersaturation vs. dry diameter measurements to infer multiple solute properties cannot be supported independently. As I explain below, it has been shown that CCN activity does not necessarily correlate with solute molecular weight. Moreover, values of some parameters must be assumed before others are inferred. These assumptions must be clearly stated so the reader understands the basis under which the remaining parameters are derived.

1a. If classical Kohler theory would hold, i.e. equations (3) + (4) apply, then CCN activity should strongly correlate with solute molecular weight, and forward calculations should agree with measurements. This is contradicted by observations. Dinar et al. (2007) report CCN activity for fractionated HULIS samples of different molecular weight ranges, termed F1 (0.2 - 0.5 kDa), F2 (0.5 - 1.0 kDa), F3 (1 - 3 kDa), F4 (3 - 10 kDa), and F5 (10 - 30 kDa). The critical dry diameter at s = 0.2% is nearly identical for F1, F2, F3 ($\sim$ 165 nm) and slightly smaller for the high MW compounds: $\sim$ 192 and 212 nm for F4, and F5, respectively. Similar discrepancies between solute molecular weight and molecular weight inferred from growth factor measurements were observed by Gysel et al. (2004), Brooks et al. (2004), and Baltensperger et al. (2005).

These observations suggest that Kohler theory with its basis in Raoult's law may not generally apply to atmospheric organic aerosol. Petters et al. (2006) suggest the use of Flory-Huggins theory, which describes water activity for aqueous solutions containing high molecular weight compounds. Based on their Figure 6 both CCN activity and hygroscopic growth become insensitive to molecular weight as suggested by the experimental studies. This implies that molecular weight and activity coefficients are correlated for high molecular weight compounds. This can also be seen from Mikhailov et al. (2004) who investigated BSA, a protein with molecular weight of $\sim$ 66 kDa. In their Figure 2 they show that the molal osmotic coefficient (which is approximately equal to the effective van't Hoff factor used in this study) is a strong function of solution molality and that values of the molal osmotic coefficient exceed 100 for molalities greater than 0.1 moles per kilogram of solvent. In the present study a value of unity was assumed introducing a potential error of two orders of magnitude on the observed molecular weights. The fact that Raoult's law does not generally apply to organic aerosols presents a theoretical limitation on the claim that KTA can retrieve molecular weights from CCN measurements that cannot be easily overcome.

1b. Another important point is that there is only limited information contained in a series of critical supersaturation vs. dry diameter measurements. As the authors state the data "are well represented with a power law consistent with a $d^{-3/2}$ dependence". A trace of critical supersaturation (s_c) vs. dry diameter (d) for one aerosol type is fitted to what the authors call INCA parameter ω to

$$s_c = \omega d^{-3/2} \tag{1}$$

This is identical to the parameterization used by Fitzgerald and Hoppel (1982) and Snider and Brenguier (2000) and also very similar to other single parameter representations of Kohler theory that have been suggested in the literature (Hudson and Da, 1996; Rissler et al., 2006; Petters and Kreidenweis, 2007; Wex et al., 2007). From this single measured quantity the authors deduce σ, M_s, ρ_s, ν (the effective van't Hoff factor containing the activity coefficient and the numbers of ions the molecule dissociates into). Clearly the solutions are not unique; an infinite number of possible combinations of σ, M_s, ρ_s, ν can produce the same ω. Some of these properties may be guessed within a factor of two, for example solute density and dissociation state, but they can certainly not be retrieved independently, even if activity coefficients and solute molecular weight (see previous comment) are not correlated. In the framework presented in the manuscript it is also assumed that mixtures behave ideally, i.e. in Equation (9) which says that if the inorganic properties are known the organic properties can be retrieved without error.

The arguments justifying the inferred molecular weights and surface tensions made in Section 3 are circular. It is first argued that the particles are not surface active (pg.

8992, see also other comments later), but then on pg. 8993, a depressed surface tension of 60 mN m^{-1} is argued for. This value is justified with the observation that the effective molecular weights inferred from this method did not otherwise agree with what was reported in Gao et al. (2004). It is never clear whether the data from Gao et al. validates KTA or if it is used to constrain the surface tension retrieval. It is then concluded that on pg. 8995 and abstract that “surfactants are likely present”, that “water soluble organics are composed of low molecular weight species with a molar mass of 200 g per mol”, and “HULIS are not an important component of the WSOC fraction”. This certainly cannot be concluded from a single measurement of ω.

2. It would be helpful to place the measurements presented here in the context of CCN activity for SOA from similar precursors published in the literature (Hegg et al., 2001; Saathoff et al., 2003; Huff-Hartz et al., 2005; VanReken et al., 2005; Prenni et al., 2007). For example hygroscopicity measured here appears significantly larger than obtained in situ for SOA sampled directly from a smog chamber. Some of the difference may be due to the different precursors and also experimental methods used (e.g. filter extract vs. online measurement, presence of an OH scavenger etc.). To compare hygroscopicity it would be useful to report equivalent single parameter fits. The values of ω reported here can straightforwardly be converted to κ values reported in Table 1 of Petters and Kreidenweis (2007) for smog chamber SOA. For $\kappa > 0.2$ (which is satisfied for the data presented here), their κ and “B” used in this manuscript, i.e. equation (3), are equivalent. Therefore

$$s_c = \omega d^{-3/2} = \sqrt{\frac{4A^3}{27\kappa}} d^{-3/2} \tag{2}$$

and thus

$$\kappa = c/\omega^2 \tag{3}$$

where $c = 1.3703 \cdot 10^{-27}$ m^3 is a constant evaluated at σ = 72 mN m-1 and 298.15 K.

3a. The XAD-8 resin column TOC technique presented in Sullivan and Weber (2006) is only sensitive to low molecular weight compounds with less than 4-5 carbon molecules. Recovery from the hydrophobic fraction is not complete and uncertain. Since only 34% (Cycloheptane), 44% (1-methylcyclohepatane) , and unknown amounts (Terpinolene) of the species are low molecular weight the WSOC number in Table 2 are misleading since the entire extract was used to generate the particles. Was the sample filtered to remove insoluble particles that may have been introduced into the solution during the sonication before atomization? If not then water insoluble and higher molecular weight compounds may have contributed to the carbon mass, but would not be accounted for in TOC analysis, potentially skewing the reported AS/extract mixing ratios.

3b. It should also be noted that the chemical analysis in Gao et al. was done using LC-MS from methanol extracts and thus the chemical speciation presented in Table 1 is not necessarily applicable to the atomized water extracts presented this study.

4. It would be helpful if the authors could include more detail in the experimental section. What were the flow ratios in the DMA? Was an impactor used? What type of charge neutralizer was used? How was the data inverted? Was the system used in scanning mode proposed by Medina and Nenes (in review) or in stepping mode as suggested in Padro et al. (ACPD, 7, 3805-3836, 2007). Since the Medina and Nenes manuscript is not available yet the current manuscript needs more information about the procedure. Why are no CCN activation curves shown? From that it may be easier to judge the quality of the data. Was there any contribution from multiply charged particles? The inset in Figure 5 and Figure 3 in Padro et al. suggest so. If so was it corrected for (and how) or not? How was the CCN instrument calibrated? What properties of AS have been assumed for the calibration (or alternatively what is the ω value for the calibration)? The uncertainties stemming from the calibration can be shown by including error bars in Figures 1, 2, 3, and 5. If these data are not readily available it may at least be helpful to estimate the uncertainty based on the work of

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Discussion Paper

Rose et al. (2007).

5. Re Section 3.4: If $\sim$ 1800 cm^{-3} deplete the vapor supersaturation disproportionately (to be noticed in the final size the instrument grows droplets) then I don't see how the maximum supersaturation in the instrument is not affected also. If true this would suggest a potentially serious problem for all studies that use the DMT instrument. This hypothesis needs corroboration from model calculations that compare the vapor flux to droplet growth rate. I did a very quick calculation assuming that 1800 droplets per cm^{-3} grow instantaneously from 0 to 6 micron at 303.15 K and an environmental supersaturation of s = 0.5%. If there is no vapor flux into the column the supersaturation drops to 0.48%. It therefore seems unlikely that the droplet growth is limited by sufficient supply of moisture.

Furthermore, since the critical supersaturation of ammonium sulfate is lower than those for SOA, particles will activate earlier in the chamber and thus ammonium sulfate droplets should grow to larger sizes, even in the absence of kinetic limitations. I can offer two possible alternate explanations that may explain why the opposite behavior might have been observed 1) particles may evaporate between the exit of the column and sizing in the optical particle counter. The temperature of the optical block is usually elevated and can be set manually. Sometimes it is set to higher values to prevent fogging of the OPC. Perhaps this was the case during the calibration? 2) The final droplet size is also an indicator for the supersaturation inside the instrument. Is it possible that for the high supersaturations day-to-day variability of the achieved supersaturation can account for the differences?

6. I have a general comment about the application of the Szyskowski-Langmuir equation to CCN activity. The activation curves are well represent with a power law $s_c = \omega d^{-3/2}$. If surface tension would be an effect there should be a deviation from this. How strongly will depend on the α and β parameter. To show that the Szyskowski-Langmuir equation applies it is necessary to show 1) how strongly the slope should deviate from the -3/2 relationship, and 2) whether or not that can be seen given the un-

certainties in the measurements. To my knowledge this has not been presented in the literature. In addition to this experimental question there are several theoretical points that are only partially discussed in the manuscript. The application of the Szyskowski-Langmuir isotherm obtained from bulk data in Kohler theory is questionable for the following reasons:

1. Partitioning may occur between the bulk and the surface of a curved droplet as was discussed by Li et al. (1998) and Sorjamaa et al. (2004).
2. Salting out may occur in the presence of some high molecular weight compounds as suggested in the manuscript. However, "salting out" seems thermodynamically tricky since it leads to an aqueous two phase system that is in thermodynamic equilibrium (Albertsson, 1971). These aqueous two-phase systems have equal chemical potentials, i.e. water activities, but also have a clear interface. How "salting out" would occur in a curved droplet has not been theoretically explored and its effects on CCN activity are not understood.
3. Micelle formation may result in little variation with surface tension with carbon concentration as was also pointed out by Tabazadeh (2005).
4. The surface tension of mixtures containing surface active and surface inactive species cannot be computed straightforwardly (Topping et al., 2005).

For these reasons a rigorous application of surface tension in the framework of Kohler theory is difficult. Unless it can be shown that Szyskowski-Langmuir isotherms can be used to accurately predict CCN activity, including for mixtures as it has been applied to in this manuscript, the surface tension term in equation (3) remains a "free" parameter that is in fact adjusted to fit the measurement (i.e. the observed ω). There is no reason to prefer one value of surface tension over another, since either density or molecular weight, or activity coefficients may counteract the effect of whatever value was chosen for the surface tension parameter.

While the above does not preclude the authors from presenting measured isotherms, which are needed to validate its applicability to measurements, I find it surprising that although no surface tension depression was measured (i.e. Figure 4), it was invoked later to explain the data.

Other comments:

1. Equation (3) is in error, either the dry particle diameter is combined with the "B" parameter as was done in equation (4) or it should appear directly in equation (3).

2. The sentence that "the aerosol transition to pure AS with a $m_i^{-1/2}$ dependence implies that there are no strong surfactants" needs to be fixed. Do you mean "the hygroscopic behavior"? Also please add the Padro et al. reference which shows this point.

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