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Atmospheric Chemistry and Physics Discussions

Interactive comment on "CCN activity and droplet growth kinetics of fresh and aged monoterpene secondary organic aerosol" *by* G. J. Engelhart et al.

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The paper is a very nice contribution to the growing body of literature examining the CCN activity of lab-generated secondary organic aerosol (SOA). Encouragingly, multiple results thus far, including the ones presented here by the authors, point to a common value for monoterpene SOA. In my opinion this is one of the most important findings and should be highlighted in the abstract and paper. As I explain in more detail below, the paper does not make enough of an effort to put the current study into context with this prior work, in the sense of quantifying the parameters needed to describe monoterpene CCN activity.

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Specific comments:

The Abstract should be rewritten. First, ”monoterpene SOA is quite active and would likely be a good source of CCN in the atmosphere.” The CCN activity of monoterpene SOA has already been established in the literature, and the important result here is that the present findings confirm the prior estimates as well as show the impacts of oxidative ageing over several hours. This statement is also not quantitative, except when linked with the last sentence that gives some parameters for representing the CCN activity (in fact I would suggest to move that sentence, modified by pointing to prior work, toward the end of the Abstract). Second, 70-80% water soluble mass is cited, whereas in the text the ”asymptotic composition” is quoted as 65% soluble material. This brings me to some confusion about the estimated molar mass. It is computed for the aerosol as a whole from KTA (assuming complete solubility, which is not consistent with the stated solubility), but in the Abstract it sounds like that molar mass is for the WSOC portion, which is clearly not the case from Figure 9 (some rewording is required).

p. 98, lines 5-8: ”Previous work on SOA”: all of the cited references here are to CCN studies of pure organic compounds, some of which may indeed be minor components of SOA. I don’t understand why they are cited as ”previous work on SOA”, when there are several studies that actually did look at SOA systems. In the sentence prior to this one, the King et al (2007) study is cited: they did actually generate monoterpene SOA, and compare their findings of CCN activity to prior work also cited here. Again those values are generally in agreement, within the experimental uncertainties, with this work and with prior work.

p. 98, l 16: ”Much lower CCN activity”: The Van Reken et al. study did find lower CCN activity toward the end of their experiment, but similar or higher near the beginning. See the plotted comparison of some of the Van Reken data against other work that appears in Prenni et al. (2007).

p. 98, l 17: The Prenni et al. study is mentioned, but unlike the discussions of the Van

ACPD

8, S434–S440, 2008

Reken and Huff-Hartz papers, no quantitative information is given about our findings. These are easily accessible, especially since we compared our data to both of those studies. The values from King et al. (2007) should be added here as well. There may be additional studies of CCN activity of monoterpene SOA that have recently appeared; the authors should check that they have gathered all of the relevant references. One issue that may arise with the intercomparison is that not all of the data are presented in a similar format as here, namely the critical dry diameter at a specified percent supersaturation. However, all of the data can be interconverted to these values. Such an update to the comparison presented by Prenni et al. would be a very beneficial addition to the literature and would serve to build confidence that monoterpene SOA CCN activity is now well-understood.

One thing that is not mentioned in this discussion of prior work is that several different methods were used to determine CCN activity. For example, Van Reken integrated the size distribution to the 50% number activated to estimate the critical diameter, while Prenni et al used monodisperse particles and either scanned size or supersaturation. Different CCN counters were used as well. These differences in experimental approach should introduce some scatter into the findings.

p. 100, l 20: ”Parameterization of the CCN properties of this important class of SOA is missing.” This statement is not true. Petters and Kreidenweis (2007) give a parameterization, in terms of kappa, of CCN activity of a-pinene and b-pinene SOA (they are the same). We include the observations of Van Reken and Huff Hartz in the estimate. The equivalent kappa values I calculate for King et al. and for this work (see below) are within these estimates.

Section 2: Experimental methods: It seems the monodisperse aerosol was generated using a 5:1 flow ratio (it is not clear from p. 102, lines 1-3 what the flow ratio was, but this is the ratio quoted earlier in this section for the SMPS). This is the same flow ratio used by Prenni et al (2007) to sample smog chamber SOA and by Petters et al. (2007) to sample aged organic aerosol from a smog chamber. In those studies, we found

ACPD
8, S434–S440, 2008

that it was necessary to account for multiply charged particles in the CCNc inversion to determine correct critical diameters, and developed the approach described in Petters et al. (AS&T, 2007). In that paper we show that the correction is most important for large critical diameters (low hygroscopicity), but depends on the input size distributions. They were measured in this study (p. 100, line 14-15) but not reported. I expect that the multiplet correction is not critical for the findings here, but the authors should explain whether it was applied, and if not, justify why it is not needed.

Also in Section 2, I may have missed a discussion of how uncertainties in the measurements were generated. This should be included. Finally, one very important consideration that I think belongs in Section 2 is described in Section 3, Results: namely, the findings for ammonium sulfate test aerosol. It is great that the authors included their data points for the salt and the values used for this species in their Kohler calculations; this information is needed to intercompare studies using different assumptions about the activity of the calibration aerosol. Using the values on page 104, I find kappa=0.72 for ammonium sulfate is assumed in this work. [Actually, it is a little unclear; kappa=0.72 is assumed for their Kohler calculations, but the measurements from the two counters are slightly above and below this value, so the calibration kappa is somewhat different between the counters and from the assumption, unless data are later corrected? The CCN counters must be calibrated because SSw cannot be predicted from the temperature measurements alone, in either instrument.] It is understood that various assumptions about the activity of calibration aerosols, primarily ammonium sulfate and sodium chloride, affect the reported CCN data (see, for example, the comprehensive study by Rose et al.). In Prenni et al., kappa=0.6 is assumed for ammonium sulfate. Therefore, there will be an offset between the reported SOA critical diameters from Prenni et al. and from any other study, including this one, that assumes a different ammonium sulfate value for the calibration.

Page 105, Section 3.2: Using the parameters from ”classical” Kohler theory given here, I compute kappa=0.15. From Figure 3, rough estimates of the variation in kappa that

ACPD

8, S434–S440, 2008

these points represent are 0.1 < kappa < 0.2 for 0.33% SSw. Especially considering the offset in calibration from Prenni et al., their value of 0.1 +/- 0.04 (as summarized in Petters and Kreidenweis, 2007) is in excellent agreement with this present estimate.

Section 3.2, Aging of SOA particles: This section is interesting, and potentially quite useful to modelers. It would be good if the information could be made more quantitative, that is, the change in critical diameter with time in the chamber is given, but the relevant parameter for the atmosphere is the equivalent atmospheric aging, which is approximated as 2 days from the ozone levels used. It is also important to note whether the aging changes CCN activity appreciably, but to evaluate this, a common framework is needed, which could be the critical diameter or the molecular weight. The effects on CCN activity of oxidative aging (although not of the same system as studied here) were experimentally investigated and discussed by Petters et al. (GRL, 2006), who expressed changes in terms of kappa variations and discussed whether the changes were sufficient to modify atmospheric lifetimes. Perhaps some of the ideas proposed there could be of use in discussing the implications of the aging observed here.

p. 104, line 26: ”a DRY density of 1.77;”

p. 105, lines19-21: The change in critical diameter in the initial part of the experiment might be due to higher uncertainty, rather than a real physical change, if low or rapidly-changing number concentrations of appropriate particle sizes are present. (The multiplet correction may be more important at the start of the experiment as well.) As the size distribution stabilizes by coagulation, there are more particles in the 50-100 nm size range, which is where the CCNc needs to sample from. Can the authors comment on this possibility?

Figure 7 is a very nice summary. I would suggest to use ln sc- ln diameter axes, because these yield nearly straight lines and the relationships are easier to see. The authors could also, similar to Prenni et al., show prior work on the same figure to demonstrate the agreement (or lack thereof) between the various monoterpene SOA

ACPD
8, S434–S440, 2008

CCN studies. I think the information shown here is essentially the same as that in Figure 14 (or could be made the same by including the 15% uncertainty in the Kohler fit parameters in the ”SOA” line in Figure 7). If that is the case, then Figure 14 is not really needed.

Section 3.4: In this section (and also Section 4, and whenever else the best-fit parameters, especially molecular weight, are quoted), ALL of the assumptions that are needed to get to an estimate of molecular weight must be clearly identified. Reported changes in molecular mass are actually changes in M/rho, which can only be interpreted as molecular weight changes if rho is held constant. Further, to derive molecular weight, it is also necessary to assume values for soluble fraction, and van't Hoff factor. Equation (2) shows this nicely because M/rho is derived, and not M directly, and epsilon, sigma and nu are parameters on the RHS that need (constant?) values before M/rho can be fit. This is not always clearly explained in the manuscript. Also, see my comment above about the assumption of complete solubility used to derive molecular weight and the stated soluble fraction. My main concern with making this presentation very clear, is in how these parameters may be applied by others, if the conditions on each are not clearly identified. For example, the estimated molecular weight could be used in a modeling study with inconsistent assumptions about soluble fraction, density, or nu, which would yield estimated CCN activities that are not in line with the experimental data.

Section 4: lines 6-8: here it is omitted that also values for vant Hoff factor and solubility have to be assumed for the parameterization.

Page 112, lines 20-23: ”similar to activation diameters estimated from classical Kohler theory”: I don't see how this is possible, since the classical theory assumes a single component with known properties, or at least multiple components with known properties. Clearly, SOA does not meet these criteria. Kohler theory was FIT to these data, as well as in prior studies, but no a priori estimate is possible. Perhaps the authors are referring to single-component organic studies. Table 1 in Petters and Kreidenweis

ACPD
8, S434–S440, 2008

(2007) attempts to summarize and compare these, for the data available up to the time that paper was prepared.

The final paragraph of the paper should be modified to reflect the comments above, namely: how this work fits in with other monoterpene studies that together already suggest a single CCN-parameter (whether that be kappa, molecular weight, or critical diameter) value for monoterpene aerosol; and how that value compares with other particle types (i.e., a more quantitative estimate of ”good CCN activity”).

Petters, M.D. and Kreidenweis, S.M., ”A single parameter representation of hygroscopic growth and CNN activity”, Atmos. Chem. Phys., 7, 1961-1971,2007.

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Petters, M. D., A. J. Prenni, S. M. Kreidenweis, and P. J. DeMott, ”On measuring the critical diameter of cloud condensation nuclei using mobility selected aerosol”, Aerosol Sci. Technol, 41, 2007.

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