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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Solid state and sub-cooled liquid vapour pressures of cyclic aliphatic dicarboxylic acids" *by* A. M. Booth et al.

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Responce to reviewer 1

We wish to thank the reviewer for their helpful comments, and we have addressed them point by point as follows, our response are denoted by –

Review of "Solid state and sub-cooled liquid vapour pressures of cyclic aliphatic dicarboxylic acids" by Booth et al. Development of predictive, empirical relationships between molecular structure and temperature dependent vapor pressures remains an important task, as such predictive relationships are used to determine vapor pressures for compounds within models of SOA formation. However, the utility of such measurements is hampered somewhat by the lack of data for very "low" volatility compounds

and for multi-functional "low" volatility compounds (i.e. the empirical paramaterizations are typically developed using compounds with vapor pressures well above the range of interest for atmospheric applications). In this manuscript, Booth et al. expand the database for vapor pressures of low-volatility compounds by focusing on cyclic aliphatic dicarboxylic acids. This study allows for the assessment of how structure affects vapor pressures, since the authors have previously determined T-dependent vapor pressures for other dicarboxylic acids with the same carbon number but different structures (e.g. linear).

Overall, the measurements appear to be of high quality. However, I find the discussion to be generally lacking in thoroughness. For example, literature data is presented that is never discussed in the manuscript (e.g. azelaic acid or the branched C7 diacids). Also, the authors focus their discussion on vapor pressures only, but they have also measured enthalpies of vaporization, which are just as important as vapor pressures. Some discussion of the enthalpies of vaporization, and in particular how they differ between linear and branched structures, should be provided. For example, are there any relationships between how delHsub changes from linear to cyclic and how the VP changes from linear to cyclic? Can the authors suggest a reason that the delHsub for 1,1-cyclopropane dicarboxylic acid is so much larger than for the other cyclic diacids considered here? For the linear diacids, delHvap generally increases with increasing carbon number (after accounting for the odd-even behavior), but here the opposite is observed. For the cyclic C7 diacid, the vapor pressure is essentially the same as for the linear variant, but the observed delHsub is much, much lower (66 vs. 147 kJ/mol). This seems to me to be worth commenting on as it is a somewhat surprising result. However, this is just one example of how the discussion could be expanded to make the discussion more complete. Once the overall discussion is flushed out further, I think that the manuscript will be publishable. Specific comments/suggestions follow below.

General Notes:

P. 23018-23019: The lengthy discussion of different VOC emissions seems somewhat out of place and distracts early on from the focus of the manuscript. The authors could much more succinctly get across their point that there are a vast number of potential SOA forming compounds in the atmosphere that come from myriad sources.

– We have cut down the 2nd paragraph of the introduction, it now reads "Significant emissions of volatile organic compounds (VOC) arise from biogenic sources and global rates have been estimated at ∼800 Tg C y-1 (Fowler et al., 2009). About 50% of the biogenic VOC emissions are thought to be isoprene (Guenther et al., 2006), monoterpenes contribute 10-15%, and sesquiterpenes are also emitted in small quantities (Fowler et al., 2009). The vast emissions of isoprene in particular, and terpenes in general means that if they yield a small amount of aerosol, then the effect on the global organic aerosol budget would be substantial (Henze and Seinfeld, 2006). Products from terpene oxidation such as pinic and pinonic acid have been found in atmosphere aerosols (e.g. Boy et al., 2004; Fu et al., 2009)."

P. 23021, L. 13: The reference to Booth, 2010 would better be to one or more of the papers that actually develop the estimation methods.

– we have changed this to "(e.g. Nannoolal 2008, Moller 2008)

Section 2.2: The discussion of the “slope” makes it seem as if there is a linear relationship between temperature and vapor pressure, which is not the case. The authors should make clearer how this temperature-adjustment is done. I assume it is some sort of Clausius-Clapeyron type equation. Also, an equation in this section might be useful. For example, the very last sentence mentions how delSvap is calculated, but it is not made clear in the discussion why delSvap how it is specifically used.

– The reviewer is correct and the relationship between vapour pressure and temperature is not linear, this dependance is encapsulated in what we refere to as the ’vapour pressure method’ the calculation of which requires different inputs for different methods (e.g. delSvap in the case of the Myrdal and Yalkowsky method). All the methods here require the boiling point to be calculated separately. We have decided against a full description of each technique as it would verbatim repeat a large section of our previous paper, so we have kept the current, rather general descriptions. We have reworded the section slightly to try and clarify this, it now reads "... The vapour pressure equations (referred to here as the vapour pressure methods) describe the vapour pressure, which varies exponentially with temperature, (see eqn 2) as a function of several inputs, such as group contribution parameters, or the vapourisation entropy. All the methods here also require the normal boiling point, Tb, to be calculated separately. Together they described the vapour pressure from 1 atmosphere at the normal boiling point down the pressure at the required temperature, in this case 298 K... "

– The end of the 2nd para in section 2.2 has been changed to "This was then used with the equations of Myrdal and Yalkowsky (1997) which uses the flexibility of the molecular structure and hydrogen bond number to estimate the entropy of vapourisation delSvap."

Section 3: I suggest adding two sub-headings, one for KEMS and one for DSC, to break up the discussion.

– Changed as suggested.

Table 2: Could probably put this in supplementary material, but up to the authors.

Table 3: Caption should indicate clearly somehow that this is not all literature observations, but only a selected subset of measurements made using particular techniques.

Table 3: For 2,2-dimethyl glutaric acid it is not clear how the values were “extrapolated to 298 K” if delHvap is not known. This should be given if it is, and if not it should be made clear how the extrapolation was done.

– In the caption of Table 3 (now 1) we have added the VP method used for each reference. The delH and delS sub for 2,2-dimethyl glutaric have now been added. We have decieded to leave table 2 in the main body. Tables 1 & 3 and 4&5 have been merged as per reviewer #2’s suggestion.

P. 23024, L. 23: It is understandable why the authors choose to use the similar Knudsen mass loss results for comparison purposes, but it is not made clear why the TDMA values are used instead of any of the other methods that were discussed in the introduction, at least for compounds where VP's derived from multiple techniques exist. This certainly should be made clear, and justified given that the various measurement techniques do not necessarily all agree. Also, the comma after "loss" should be a semicolon and references given for the TDMA measurements.

– For the literature branched and cylic diacids, there are only the HTDMA results of the Bilde group and the Knudsen mass loss of Riberio da Silva's group to compare to. For the straight chain diacids there are a large number of results from different methods, we have used our own where available (up to C6). We have used those of Bilde for C7 and C8 as we seem to be in fairly good agreement with their C4-C6 striaght chains, this is to make the comparisons between our cyclics and the striaght chains as consistent as possible. We have added this rationale to the text.

Figure 3: I recommend the authors use color within the figure to help visually distinguish between the measurements made using different techniques. The +, , x's work to some extent, but I think color would make the picture a lot clearer.

– We've kept the symbols and added colour to distinguish between the techniques

Section 4.1.2: The authors state that "1,1 cyclobutane, adipic, 2-methyl glutaric and 3-methyl glutaric, show the same solid state vapour pressure for the cyclic and branched, but the straight chain results are lower by two orders of magnitude." Then, later they state "The sub-cooled liquid vapour pressures, compared to the C6 cyclic compounds show 20 a $\sim$3 fold reduction for the straight chain and a 1.5 factor increase for the branched." However, if one looks at the figure, the difference between the cyclic and branched between solid and liquid particles is effectively identical. Therefore, it does not seem fair or consistent to say that in one case they "show the same" vapor pressures but in the other they show a "1.5 factor increase." The discussion should be adjusted to be self-consistent.

– We have changed the first statement to read the branched diacid is approximately 1.5 times more volatile than the cyclic.

Section 4.1.3: No discussion is given regarding the VP's of the other branched (as opposed to linear and cyclic) C7 diacids. Either some discussion should be added or they should be removed from Figure 3. In other words, why present them if they are not going to be discussed Similarly, there seems to be no reason to include values for azelaic acid (the linear C9 diacid) in the tables or figures. For one, no discussion is given regarding this compound and also the focus of this paper is on the cyclic diacids and no measurements are presented for a cyclic C9 diacid. So the inclusion of the C9 diacid seems completely out of place (unless, or course, the authors wish to provide some context).

– We have now added a short discussion on the solid state dimethyl glutarics & methyl adipic, "The branched C7 diacids do not have the literature data for Tm and delHfus to do a sub-cooled liquid correction so only the solid state are available. 3-methyl adipic acid and 2,2-dimethyl glutaric acid have roughly the same vapour pressure, which is 3 times higher than the C7 straight chain and cyclic diacid. 3,3-dimethyl glutaric acids is much more volatile with a vapour pressure 15 times that of the other two branched C7 diacids." The azleaic acid has been removed from figure 3 and table 5 & 7.

Section 4.1.4: The statement "The lower solid state vapour pressure for 1,2 cyclopentane dicarboxylic acid may be explained simply by that compound having a more stable crystal structure" is ambiguous. Lower than what And I thought that the authors just got done arguing that crystal structure effects are not important for the cyclic diacids. Whether they are or are not, there is a lack of self-consistency in the discussion.

– We have reworded this to "The slightly lower solid state vapour pressure for 1,2 cyclopentane dicarboxylic acid compare to the other cyclics may be explained simply by that compound having a more stable crystal structure, but that does not explain the difference in sub-cooled liquid vapour pressures which are independent of crystal structure effects. ". The crystal structure has a significant effect on the trends in the solid state vapour pressures, but not the sub-cooled. The C7 cyclic sub-cooled VP is about half that of the C6 and C8, but it is not orders of magnitude lower as is the case with the straight chain diacids.

Table 7: The authors should include in this table the ratio between the measured and modeled (or the inverse) to facilitate easy comparison. This value could be placed, for example, in parentheses after the vapor pressure. In fact, I would argue that the ratio is the more important parameter in the context of this manuscript than the absolute vapor pressure and thus, if anything, the table could be filled with the ratio model/measurement ratio rather than the model VP's.

– We have changed table 7 (now 5) as suggested to include the absolute VP and the ratio between it and the measured.

Table 7: Presumably, the models also predict delHvap in order to allow for movement from the boiling point to 298 K. A comparison between measured and calculated delHvap would be useful.

– We have inserted a table of estimated delHvaps and have added the following discussion to the text. "Table 6 shows the estimated enthalpies of vapourisation (?Hvap = ?Hsub - ?Hfus) compared with those from KEMS/DSC measurements. Barley and McFiggans (2010) in their study of vapour pressure methods noted that most of the error for the methods they looked at came from the estimation of the boiling point, and enthalpy of vapourisation estimates were generally much easier to get right. The Moller/Nannoolal and Nannoolal/Nannoolal methods here both use the same boiling point, but for most of the compounds there is an order of magnitude difference in the predicted P298 which can only come from the difference in predicted ?Hvap between them, this should not be a complete suprise however as the changes to the Nannoolal et al., (2008) method that the Moller et al., (2008) is based on come from extra terms for carboxylic acids, which will obviously have a big impact for the diacids.

The different methods show consistent bias in ?Hvap for the diacids measured in this study. The Moller et al., (2008) method, excepting levoglucosan, always estimates a higher value for ?Hvap than Nannoolal et al., (2008) which predicts higher ?Hvap values than Myrdal and Yalkowsky (1997). The ?Hvap estimates seem very good for the C5 diacids (typically within 20 KJ mol-1 or less) but as the number of carbon atoms in the molecule increases the behaviour of the straight chain and cyclic diacids diverge. ?Hvap increases with carbon number for straight chain diacids and ?Hvap decreases with increasing carbon number for cyclic diacids. The estimation methods however, do not significantly change their estimates, for example there is only a range of 23 KJ mol-1 between the highest and lowest estimate for ?Hvap using the Nannoolal method, but the experimental methods vary by 106 KJ mol-1. In spite of this the estimation methods can sometimes give good P298 values, as opposing errors in ?Hvap and Tb can cancel out. "

Levoglucosan: The authors comment that the Moller method is the most inaccurate, being 3 orders of magnitude off of the measured values. But really, the more important aspect seems to me to be that all methods are off by 1-2 orders of magnitude, i.e. they are all bad!

– The reviewer is correct, the best that can be said for the other two methods is they are less wrong! we have added "although it should be noted that all the methods perform badly with this compound." to the end of the paragraph to emphasize this.

Tables 4 & 5: It could be interesting to add a column that gives the ratio between the sub-cooled and solid vapor pressures, for easy comparison.

– Changed as suggested

General: It could be interesting to have a more complete discussion of measurement accuracy vs. precision. The authors calibrate their KEMS system using a particular compound, but if one considers values for malonic acid vapor pressures in the literature it is clear that reported values range over an order of magnitude, much larger than the +/- 40% stated as the maximum error. Certainly, this value must be a measure of the precision of the measurement, and not the absolute accuracy, since the accuracy can only be as good as the calibration compound used. Noting that the KEMS measurements for malonic acid vapor pressures are on the “high” side of the literature values, this suggests then that the KEMS may (and I emphasize may, as opposed to does) have a bias in a particular direction simply because of the calibration compound used. It’s certainly possible that the KEMS measurements are the most correct (with biases in the other measurement techniques), but this is (unfortunately) not known at this point. I only bring this up because this has implications for the comparison with the theoretical VP values. Just something to consider.

– KEMS is a relative technique and the reviewer is correct in saying it can (in absolute terms) only be as good as the reference used. The errors we quote are the random errors from repeat measurements and it is true that is does not address any possible systematic errors with this technique specifically, or as they tend to aggree with the results of Riberio da Silva et al., (1999) effusion methods in general. As suggested by reviewer 2, we have included the VP as a function of temp we used for our malonic acid calibration, as the technique is relative, it will be possible for the reader to change the results should a systematic bias become evident.

– Additional Changes

– On delH. We had now discussed the differences in measured delH(sub) values, between the analagous straight chain and cyclic acids. We have added "The enthalpy of sublimation, delHsub, decreases rapidly as the ring size increases, from 126 KJ mol-1 for C5 to 66 & 67 KJ mol-1 for C7 and C8 respectively. The C5 straight chain diacid has a similar delHsub to the cyclic, 123 vs. 126 KJ mol-1, but the pattern for straight chain diacids shows an increasing delHsub as chain length increases from 123 KJ mol-1 for C5 to 184 KJ mol-1 for C8. This makes for a substantial difference of 117 KJ mol-1 between the cyclic and straight chain C8 diacids. The widening gap with increasing carbon number between the delHsub for straight chain and cyclic acids

may be of consequence for thermal desorption measurements of mixtures of cylic and branched acids as compounds with similar sub-cooled liquid vapour pressure and O to C ratio could have very different results after thermal processing and undesired distillation could occur." We discuss delH vap within the context of the estimated values (see above).

– On Levoglucosan. The transition we reported at 385.7 K may in fact be a phase transition between two solid states, with a true melting point at 456 K, we have applicd the prausnitz correction to both these phases in table 3, and we compare them with literature measuremens above and below this solid transition (Oja and Suuberg), as well as liquid phase measurements (Epshtein). The estimated vapour pressures for levoglucosan are now compared with the measured vapour pressures after being corrected for both the 385.7 and 456 K transitions. We have added "Levoglucosan exhibits a solid phase transition at 385.7 K and a melting transition with a small enthalpy of fusion at 456 K (Oja and Suuberg, 1999), we have used the correction in equation 1 to adjust for both these transitions and arrive at a final sub-cooled liquid vapour pressure. Oja and Suuberg (1999) have measured levoglucosan below and above this transition getting vapour pressures of 1×10-5 and 1×10-4 Pa respectively. The first is about a quarter of the value we measure, whereas the the vapour pressure after the transition agrees with our value of 1.35×10-4 Pa within error. Epshtein (1964) has measured levoglucosan from 468 to 528 K, extrapolation of their values down to 298 K gives a vapour pressure of 1×10-3 Pa which is about 5 times higher than our final sub-cooled liquid vapour pressure of 1.93×10-4 Pa, although it should be noted that this extrapolation is for a two parameter Antoine equation fit 200 K above the desired temperature." to the end of section 4.1.4

References

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