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Atmospheric
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Discussions

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

A. M. Booth et al.

alastair.booth@manchester.ac.uk

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Responce to reviewer 2

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. 2010

This manuscript presents solid state vapour pressures of a series of molecules of atmospheric relevance (cyclic aliphatic dicarboxylic acids levoglucosan) as a function of temperature. The measurements have been done using Knudsen Effusion Mass Spectrometry. Melting points and enthalpies of fusion were measured using Differen-

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tial Scanning Calorimetry. For comparison, a number of estimation methods were used to calculate vapour pressures. Prediction of organic aerosol yields and mass loadings is currently limited by lack of thermodynamic data, in particular vapour pressures and enthalpies of fusion. The data provided in this manuscript are therefore timely and relevant. The measurements seem to be of good quality. The manuscript itself is however not satisfactory and should be improved, in particular the resentation of data, the comparison with literature data and the discussion. See detailed comments below.

Introduction: The paragraph on isoprene emission and the Master chemical mechanism appears out of context. Some things are repeated many times (For example that cis-pinonic acid is a biogenic oxidation product (page 23019 line 18-19, page 23020 Line 13 and line 25)). It could be mentioned in the introduction why both solid state and sub-cooled liquid vapour pressures are relevant.

– We have cut down the 2nd paragraph of the introduction (see responce to reviewer #1), we have removed the multiple reference to the biogenic origin of cis-pinonic acid. In the 3rd para of the introduction we do include why the sub-cooled liquid is required for atmospheric studies.

Section 2.2: The authors could consider showing the simple phase diagram they refer to in the text. The last paragraph is difficult to follow, I suggest rephrasing it.

– We have reworded this section, see responce to reviewer #1

Experimental: The KEMS technique relies on calibration using a reference compound. The authors have chosen malonic acid. Since there are deviations in the literature between reported vapour pressures of malonic acid the authors should provide the vapour pressure (vs.temperature) they have used for malonic acid. Page 23024: The last paragraph is unclear – what is meant with “those compounds” (line 13)

– We used values we measured for malonic acid from a previous paper, ln P = 29.54-11058.97/T. Please see responce to review #1 for a discussion of random vs. system-

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atic errors in the KEMS. The C3-C6 diacids, which were used to get the sensitivities and errors on the sub-cooled liquid corrections, we have replaced "those compounds" with C3-C6 diacids to clear it up.

Results and discussion: The dH values are almost not discussed at all in the different sections, this should be done. I suggest to merge Table 1 and 3. It would be much clearer for the reader to see the literature data together with the results in the current work. Likewise tables 4 and 5 could be combined. Also, the tables could be organized in the same way as the figures (C5 acids together, C6 diacids together etc).

– Please see responce to reviewer #1 for a disscussion of the delH values and our changes. We have merged table 1 & 3, and 4 & 5.

How was the error of 40% on the solid state vapour pressures and 75 % on the sub-cooled liquid state vapour pressures obtained?

– The error on the solid state is based on repeated measurements of the straight chain diacids in Booth 2009, the sub-cooled liquid error is from Booth 2010 and is the total error from the solid VP, the assumption of delS(fus)=delCp, and the change from using the highest and lowest values for delH(fus) and Tm we could find in the literature. We have added this to the text.

It says that dSfus was measured, but I assume it was calculated from measured values of dHfus and Tm?

– This is correct, we have added delcp,sl = delSfus is used in this work, which is calculated using DSC measurements and delSfus = delHfus/Tm.

Table4: The subcooled liquid vapour pressures were inferred from other measured properties and rely on a correct determination of p(solid). This should be made clear from the text/ heading of the table.

– We have changed the table 4 legend to "Sub-cooled liquid vapour pressures, melting points, enthalpies and entropies of fusion from DSC measurements and correction of

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solid vapour pressures in table 1. Estimated maximum error on P298 sub-cooled ± 75%."

4.1.1: It says that the subcooled liquid vapour pressure are free of crystal structure effects and then in the next line the smaller difference in crystal structure effects is inferred , this two statement seems contradictory?

– We mean that as there are only small difference between the solid for each C5 there are no major crystal structure effects, and that the differences match those of the scl vp, it confirms it. We have reworded this section to "The aliphatic C5 diacids; 1,1 cyclopropane dicarboxylic, glutaric and 2-methyl succinic acid, decrease in solid state vapour pressure by a factor of 1.4 for cyclic to straight chain and 1.7 for straight to branched, these are similar to the reported errors of ± 40%. The sub-cooled liquid vapour pressures, which are free of crystal structure effects, show a similar reduction (∼1.6) from cyclic to straight. The differences between the C5 acids as solids are similar to those as sub-cooled liquids, which indicates the crystal structure effects for these solids are negligible."

The odd-even effect and crystal stability: a more original reference for example to Thalladi et al.2000 should be given instead of Booth et al. 2010.

– Changed as suggested

Given the large uncertainties (40%) it seems that the straight chain and the branched C5 acids have the same vapour pressures. A similar comment to the comparison of sub-cooled liquid vapour pressures where the uncertainty is 75%.

– We have reworded that section (4.1.1) saying the differences are similar to the reported errors, see above.

4.1.2: The subcooled liquid vapour pressures obtained in the current manuscript should be compared with subcooled liquids vapour pressures obtained from EDB and TDMA techniques (at least glutaric and adipic acids are available).

– We have deliberate used similar techniuques where possible to try and make the comparisons which the cyclics more consistent.

4.1.4: I do not understand the text in this section. It does not explain what the trends are. Also it says that the vapour pressures falls from C3 to C5- but C3 and C4 are not shown in the figures or tables?

– The descriptions had refered to the ring size, where as the graph referes to the size of the molecule as the branched and straight chain do not have rings, to avoid confusion we now only refere to the total carbon number in all cases, we have reworded this section to "The sub-cooled liquid vapour pressure shows a similar trend to the solid state vapour pressures but are even closer to each other, within error the C5, C6 & C8 sub-cooled liquid vapour pressures are the same. The solid state vapour pressure falls from C5 to C7 and rises by C8. 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 following could be addressed: Why is the vapour pressure of azelaic acid (C9) subcooled higher than the subcooled liquid vapour pressure of suberic acid (C8). Why is C9 not discussed in the text?

– As we do not have a C9 cyclic we have removed all reference to azelaic in the tables, figure and text.

It seems that except for C5 the cyclic dicarboxylic acids have the same subcooled liquid vapour pressure within experimental uncertainties. This could be mentioned in the text.

– Agreed, we have reworded this section.

Minor Line 25 I suggest to insert “experimental”: “There are several experimental methods.”

– Changed as sugggested

Abstract, l 3: I suggest to rephrase to “Additionally the solid state pressures of the atmospherically . . ..” I suggest to give the temperature range of the measurements.

– Changed as suggested

– Please also see the note concerning Levoglucosan phase transitions in responce to reviwer #1.

References Pope et al. J. Phys. Chem. A 2010, 114, 10156, Riipinen et al. J. Phys. Chem. A 2007, 111, 12995, Thalladi, V. R.et al. J. Am. Chem. Soc. 2000, 122, 9227.

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