

## ***Interactive comment on “Thermodynamic properties and cloud droplet activation of a series of oxo-acids” by M. Frosch et al.***

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A review of "Thermodynamic properties and cloud droplet activation of a series of oxo-acids" by M. Frosch, A.A. Zardini, S.M. Platt, L. Müller, M.-C. Reinnig, T. Hoffmann, and M. Bilde.

The paper presents CCN counter, TDMA and LC/MC results of oxo-dicarboxylic acids. The authors determine the CCN activity of the oxo-acids and also derive solid state vapour pressures. They also observe the decarboxylation of beta oxo-diacids in aqueous solutions, explaining why they have not been observed in the atmosphere.

General Comments: The paper is very well written and presents some interesting results. There is a big need for more vapour pressure data for low-volatility multifunctional

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organics and the paper is the first one to my knowledge addressing this for keto-diacids. It would have been interesting to compare the results to vapour pressure estimation methods, getting multifunctional compounds right is an important challenge. The authors should be commended for the combining of multiple techniques to tell a coherent story. It address the all the relevant properties; vapour pressure, CCN activity and the chemical reactions of a class of compounds which haven't recieved much attention.

The paper clearly merits publication, subject to the following points being addressed.

1. Section 2.1 concerning alpha and beta positioning: Wouldn't oxo-succinic acid normally be described as alpha? Couldn't you describe it as either?
2. Section 2.1 2nd para with keto-enol, line 21 & Fig 2. Does this mean that 10-30% is in the enol/hydrated form? How will this effect the vapour pressure?

Also one of the great strenghts of HTDMA in my opinion is the ability to measure mixtures. Would it be possible to control the pH of the mixture to control the keto-enol ratio in a future experiment?

3. Section 2.2 I agree that limited solubility should not be a problem with oxo-diacds, but do the authors have a feel for the solubility limits/sorts of molecules at which it should be included?

A similar question for using pure water surface tension... Can the authors comment on when (if at all) it may become important?

4. Section 2.2 eqn (2): The authors use the van't Hoff factors for calculating the water activity, Koponen et al., (2007) experimented with a couple of different methods for deteriming activity for this sort of experiment and saw a large difference for some molecules (malonic acid) and a much smaller one for succinc and glutaric acid. Can the authors comment on how much of an impact they would expect different activity coefficient methods to have on the results for the oxo-acids studied.

5. Section 3: What effect will impurities have on the reported vapour pressure? Will

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the effect be in proportion to the mole fraction of the impurity as with Raoult's law?

6. Section 2.3 or 3.2 When citing the evaporation rates and TDMA it may be helpful to have all the references in the same place (Bilde & Pandis 2001, Bilde 2003, Monster 2004, Koponen 2007, Riipinen 2007) to help the reader find all the previous results with this technique, either in sec 2.3, 3.2 or both.

7. Section 4.4: In 7, the oxo-succinic acid is reported at 294.27 K but table 4 reports the same value at 296 K, which is correct?

8. Was it possible to measure the evaporation rates over a range of temperatures? If it was then  $\Delta H(\text{sub})$  and the range should be reported.

9. How do the authors know that the vapour pressures are solid state, rather than sub-cooled liquid? I would say it definitely is solid state as the glutaric acid vp is higher than succinic acid (odd-even effect). But something should be added to the text.

10. Although it post-dates this work, it may be useful to compare with the results recently published in ACPD of Booth et al., 2010

Booth, A. M., Barley, M. H., Topping, D. O., McFiggans, G., Garforth, A., and Percival C.J.: Solid state and sub-cooled liquid vapour pressures of substituted dicarboxylic acids using Knudsen Effusion Mass Spectrometry (KEMS) and Differential Scanning Calorimetry, *Atmos. Chem. Phys. Discuss.*, 10, 5717-5749, 2010.

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