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

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We thank Alastair M. Booth for his useful comments and suggestions. We have made several corrections; a list of detailed answers to each Reviewer comment is given below:

Comment: 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?

Response: Regarding α- and β-positioning of oxo-succinic acid, the following changes have been made (page 3758, lines 9-12):

Old version: “The chemical structures of the organic acids studied herein are shown in Fig. 1. Note that oxosuccinic acid and 3-oxoglutaric acid have the oxo-group in the

β-position, and that 2-oxoglutaric acid and 4-oxopimelic acid have the oxo-group in the α- or ω-position, respectively.”

New version: “The chemical structures of the organic acids studied herein are shown in Fig. 1. Note that 3-oxoglutaric acid has the oxo-group in the β-position, and that 2-oxoglutaric acid and 4-oxopimelic acid have the oxo-group in the α- or γ-position, respectively. The oxo-group in oxosuccinic acid is in both an α- and a β-position. Oxosuccinic acid undergoes the reactions of a β-oxo-acid described below and is therefore characterized as such in the following.”

Comment: 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?

Response: Additional text has been inserted in the paragraph to specify the ratios between keto-, enol- and hydrates forms and the effect on vapor pressure (page 3758, line 21): “(. . .) with the enol- or the hydrated form comprising the remaining 10-30%.”

Furthermore, we add the following text (page 3758, line 25): “The position of the equilibrium between the three forms is likely to influence vapor pressure of oxosuccininc acid, since the alcohol groups of the enol- or hydrated forms are better acceptors/donors of hydrogen bonds than the oxo-group of the keto-form. The keto-form is therefore likely to have the highest vapor pressure, although magnitude of the differences in vapor pressure between the three forms is unknown.”

Comment: 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?

Response: This is a very interesting suggestion which we will consider for future work.

Comment: 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?

Response: A more quantitative discussion regarding the importance of solubility has been added to Section 2.2. We have made the following changes (page 3760, lines 10-11):

Old version: “Critical supersaturations were calculated using Köhler theory. All molecules studied have a high solubility in water and limited solubility was not accounted for.”

New version: “Critical supersaturations were calculated using Köhler theory. Limited solubility was not accounted for. Following the equations provided in Bilde and Svenningsson (2004), the minimum solubility necessary for particles with diameters in the range 30-130 nm to be fully dissolved was calculated for each of the studied compounds. The solubilities of the dicarboxylic acids are available in literature (e.g. Saxena and Hildemann, 1994; Lide, 2004) and the solubilities of the oxo-acids were tested in the laboratory simply by dissolving known amounts (larger than the calculated minimum amount) of acid in water. For each compound, the actual solubility was found to be above the calculated solubility limit.”

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

Response: Some considerations about the importance of surface tension have been added to the manuscript. The following changes have been made (page 3760, lines 19-23):

Old version: “In this work we approximate σl,air and l by the surface tension (0.07275Nm$-$1) and density (997.96 kgm$-$3) of pure water, respectively. The temperature is assumed to be room temperature, Troom=298.15 K. The maximum of S (as a function of Dp) defines the so-called critical supersaturation, SSc.”

New version: “In this work we approximate l by the density (997.96 kg m-3) of pure water. The temperature is assumed to be room temperature, Troom = 298.15 K. Information about the surface tension is only available for some of the parent dicarboxylic acids (Varga et al., 2007), which are not strongly surface active. However, a good agreement between measurements and Köhler theory can be achieved using the surface tension of pure water for particles containing the salts of fatty acids (Prisle et al., 2008). Therefore, the surface tension σl,air is here approximated by the surface tension of pure water (0.07275 N m-1). The maximum of S (as a function of Dp) defines the so-called critical supersaturation, SSc.”

Comment: 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.

Response: CCN activation takes place in very dilute aqueous solution droplets (solute concentration is in the range of millimoles/L) and the mole fraction of water will be very close to 1. The deviations observed by Koponen et al., (2007) are at much higher concentrations (or lower mole fractions of water), so we expect the impact of using different methods to be minimal.

Comment: 5. Section 3: What effect will impurities have on the reported vapour pressure? Will the effect be in proportion to the mole fraction of the impurity as with Raoult’s law?

Response: We estimate the effect of impurities on the reported vapor pressure to be proportional to the mole fraction and therefore quite small. Impurities as a source of errors have been specified on page 3771, line 1.

Comment: 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.

Response: We have made the following changes; Page 3765, line 22:

Old version: “Evaporation rates were measured using a modified tandem differential mobility analyzer system (TDMA) which have previously been described in Bilde et al. (2003) and Koponen et al. (2007).”

New version: “Evaporation rates were measured using the modified tandem differential mobility analyzer system (TDMA), which have previously been described in Bilde et al. (2003) (see also Mønster et al., 2004, Koponen et al., 2007, and Riipinen et al., 2007, for results obtained with the laminar flow reactor used in this work; see also Bilde and Pandis, 2001, for the use of a similar TDMA).”

Comment: 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?

Response: The Reviewer is correct. We noticed some mismatch between the body of the text and Table 4. A new column with temperatures has been added and the values in the text corrected.

Comment: 8. Was it possible to measure the evaporation rates over a range of temperatures? If it was then del H(sub) and the range should be reported.

Response: Evaporation rates have not been measured over a range of temperatures, although it would be possible in a future set of experiments.

Comment: 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.

Response: The Reviewer is correct that we do not have a direct measurement of the particle physical state. Our assumption of dry particles are based on experimental conditions, namely the use of silica gel dryers and the low water vapor in the gas

phase, RH<6%. Moreover, as the Reviewer notices the vapor pressure values are a posteriori consistent with our assumption of dry particles. Unfortunately, this cannot be related to hygroscopicity / physical state transitions measurements of the particles, since they are, as far as we know, missing in scientific literature.

We added the following text (3766, line 14): “We did not perform direct measurements on the physical state of the particles. The assumption of dry particles is based on the experimental conditions, namely the use of silica gel dryers and the low water vapor in the gas phase. Moreover, the vapor pressure values are a posteriori consistent with the odd-even alternation effect observed in similar studies using the same apparatus (Bilde et al., 2003). Measurements of hygroscopicity and physical state transitions of the oxo-acids are lacking in the literature, and would be therefore desirable to assure we are dealing with dry particles”.

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

Response: We add the following text (page 3771, lines 16): “A related article has been recently published (Booth et al., 2010) where the authors use a Knudsen cell based method to extrapolate solid state vapor pressure at T=298K. Relevant to our work, they report results for oxo-succinic, and 2- and 3-oxoglutaric. However, only the vapor pressures of 2-oxoglutaric acid can be compared, as 3-oxoglutaric and oxo-succinic acid undergo decarboxylation in aqueous mixtures (see previous Sections). They also observe a reduction (about a factor of 3) in vapor pressure of 2-oxoglutaric compared to glutaric acid. Yet, considering the experimental errors, they report a vapor pressure which is at best almost the double of ours. The disagreement may be related to the different temperatures of the experiments (about 4 degrees) but also differences in the two techniques should be explored in the future.”

Since the Reviewer is also the author of the suggested paper which is subsequent to our publication, and reports enthalpy values, maybe a more consistent comparison can be attempted in that paper considering the temperature difference.

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 3755, 2010.