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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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General Comments

Frosch et al. report the thermodynamic properties of several oxo carboxylic acids: oxosuccinic, 2-oxoglutaric, 3-oxoglutaric, and 4-oxopimelic acids. A key finding is the reported 10-fold decrease in vapor pressure due to the presence of a carbonyl group in the α position relative to the parent dicarboxylic acid. Although the paper in general

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is very interesting and it should be published, the authors seem unaware of recent relevant literature that could improve the scientific value and relevance of the manuscript and therefore should be included in the final version. We would suggest a revision with additions, corrections and clarifications according to the points of this review prior to acceptance. We would suggest a revision with additions, corrections and clarifications according to the points of this review prior to acceptance. In page 3757, the authors state that the effects of decarboxylation and enolization have not been considered on cloud droplet formation. Closely related problems have actually been studied for the related oxo compound pyruvic acid in our group with relevance to atmospheric processes (Guzman, et al., 2006a,b,c and 2007, and Rincon et al., 2009 and 2010). In those articles we presented evidence to describe observable properties with atmospheric relevance. We presented extensive laboratory work based on a suite of experimental techniques that provided fundamental physical and chemical information. The last statement in the abstract implies the authors found that β -oxocarboxylic decarboxylation occurs in aqueous solutions, which is a well known fact. We think this statement should be written differently. As an example we measured the kinetics of β -oxocarboxylic acid decarboxylation in our studies (Guzman et al., 2006b, 2007 and Guzman and Martin 2008). Whereas the experimental methods have been described, the analyses used in this study should be presented more carefully. In particular, details on the determination of the pK_a's are needed. The manuscript should give an indication of the uncertainties on those measurements. In pages 3785 (Table 1) and 3765 the authors report pK_{a1} = 2.4 and pK_{a2} = 4.9 values for 2-oxoglutaric, which differ from the 2.47 and 4.68 values reported in the Handbook of Chemistry and Physics (Lide, 2008), respectively. The text should be corrected to account for this oversight.

Specific Comments

Page 3757, lines 22-24

Rissman et al., (2007) states that oxosuccinic acid, also called oxalacetic acid, is a “surrogate” standard used in chemical analyses to identify species in SOA. The use of

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the word surrogate is recommended as it was chosen for having similar mass, retention time (in gas or liquid chromatography methods), and functional group as the species present in SOA.

Page 3759, lines 1-5

Decarboxylation of β -oxocarboxylic acids can also be catalyzed by zinc ions and we have recently studied the temperature dependant rate of decarboxylation of axaloacetate (or oxosuccinate) to pyruvate, which followed an Arrhenius behavior (Guzman and Martin, 2008).

Page 3765

The supplementary material present titration curves for 2-oxoglutaric and 4-oxopimelic acids but there is no information about the procedure, e.g. the concentrations of sodium hydroxide standard and oxo carboxylic acids used.

Page 3774

The authors should take into account the kinetics parameters of the references cited earlier in the paper and consider the timescale of the experiment and how fresh the sample was. It appears that the measurements correspond to pyruvic acid, the product of decarboxylation of oxosuccinic acid (Guzman and Martin, 2008). The results suggest that the sample was decomposed prior or during the experiment and the conclusion would not be valid for oxosuccinic acid.

Page 3775 and Page 3793 (Figure 5)

The proposed products from the reactions of oxosuccinic acid (citroylformic and 4-hydroxy-4-methyl-2-oxoglutaric acid) can be discarded if they are not observed in the LC-ESI-MS spectra of figure 17. Examples of products identification from the related compound Pyruvic acid are provided in the literature, where liquid chromatography with UV and ESI-MS detection, complemented by collisionally induced dissociation and 2H and 13C isotope labeling experiments where used (Guzman et al, 2006b).

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Page 3776, line 5

Why is it mentioned atmospherically relevant here again? It was stated earlier in the paper that neither oxosuccinic acid nor 3-oxoglutaric acid have been detected in atmospheric aerosols

Page 3776, lines 23-25

The loss of 3-oxoglutaric acid and oxosuccinic acid by decarboxylation can be quantified and correlated with the results by the LC-ESI-MS analysis reported by the authors. Now, if the authors assume both oxo carboxylic acids have already decomposed in the atomizer bottle, maybe they should remove the data for these particles from the paper.

Page 3785 (Table 1)

There is no supplementary information for the titration curve of 3-oxoglutaric acid to obtain pKa1 or its value in Table 1 refers the wrong citation.

Page 3789

The structure of oxaloacetic acid (oxosuccinic acid) presents the wrong numbers.

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

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