

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 express our thanks for the interesting comments. We also appreciate the references to the extensive studies on decarboxylation of the monovalent carboxylic oxo-acid, pyruvic acid. These processes, which are related to the spontaneous decarboxylation of dicarboxylic oxo acids from our study, and the influence thereof on the physical properties of pyruvic acid particles are very interesting with regard to atmospheric conditions and could be the subject of a future study. We have cited the study by Guzman and Martin, 2008. The other suggested references mainly focus on spontaneous and photo induced decarboxylation of pyruvic acid and related compounds, which is slightly outside of the scope of this study. We have carefully considered all suggested revisions and have the following comments:

C2823

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 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.

Response:

The statement on page 3757, lines 24-26 has been modified:

Old version: “It has been demonstrated that oxosuccinic acid particles can act as cloud condensation nuclei (Rissman et al., 2007), but so far the effects of enolization and decarboxylation on cloud droplet formation have not been considered.”

New version: “Rissman et al. (2007) demonstrated that oxosuccinic acid particles can act as cloud condensation nuclei, but did not consider the effects of enolization and decarboxylation on cloud droplet formation.”

C2824

Comment:

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).

Response:

The last statement of the abstract has been modified as follows, Page 3756, lines 12-13:

Old version: "Dicarboxylic acids with an oxo-group in the β -position were found to decarboxylate in aqueous solution."

New version: "Dicarboxylic acids with an oxo-group in the β -position decarboxylate in aqueous solution which affected our measurements and findings."

Comment:

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 pKa'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.

Response:

Experimental details have been added to Supplementary Material; the experimental error has been estimated and compared to the values reported by Lide. The following changes were made (page 3765, lines 1-7).

C2825

Old text: "The acid strengths of the 2-oxoglutaric acid and 4-oxopimelic acid could not be found in literature and were estimated by titration with NaOH using a combination electrode (Radiometer Analytical), calibrated using two buffers with pH 4 and 7, and connected to a PHM82 Standard pH-meter. Titration curves can be found in Supplementary Material (<http://www.atmos-chem-phys-discuss.net/10/3755/2010/acpd-10-3755-2010-supplement.zip>)."

New text: "The acid strengths of the 2-oxoglutaric acid and 4-oxopimelic acid were estimated by titration with NaOH using a combination electrode purchased from Radiometer, calibrated using two buffers with pH 4 and 7, and connected to a PHM82 Standard pH-meter. Titration curves can be found in Supplementary Material (<http://www.atmos-chem-phys-discuss.net/10/3755/2010/acpd-10-3755-2010-supplement.zip>); the uncertainties on pKa-values represent 10% (estimated). The acid strength of 4-oxopimelic acid could not be found in literature. The acid strengths of 2-oxoglutaric has been reported as $pK_{a1} = 2.47$ and $pK_{a2} = 4.68$ (Lide, 2004) and are thus within experimental error of the values determined in this study ($pK_{a1} = 2.4 \pm 0.2$ and $pK_{a1} = 4.9 \pm 0.5$; see Table 1)."

Specific Comments

Comment: 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 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.

Response: Page 3757, line 23: The word "surrogate" has been added as suggested.

Comment: Page 3759, lines 1-5

Decarboxylation of β -oxocarboxylic acids can also be catalyzed by zinc ions and we

C2826

have recently studied the temperature dependant rate of decarboxylation of axaloacetate (or oxosuccinate) to pyruvate, which followed an Arrhenius behavior (Guzman and Martin, 2008).

Response: As suggested, the following text has been added (page 3759, line 2): "(...) zinc (Guzman and Martin, 2008), (...)"

Comment: 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.

Response: Information about concentrations has been added to Supplementary Material as suggested.

Comment: 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.

Response: Kinetics and rates of decarboxylation of both oxosuccinic acid and 3-oxoglutaric acid are discussed in Section 2.1. We have added the following text (page 3760, line 8): "Assuming decarboxylation to be a first order pH dependent reaction, the rate constant can be estimated to be $\sim 10^{-4}$ min⁻¹ at room temperature and pH = 7 (Larson and Lister, 1968)."

Furthermore, the following text is added to elaborate on the time scales of experiments (page 3767, line 19): "Fresh aqueous solutions for the atomizer were prepared each morning and used the entire day."

C2827

We agree that the conclusions are valid for the products of decarboxylation and aldol condensation of the β -oxo-acids. This is stressed in the sections containing the Results and Discussion and Conclusion, as well as in the last statement of the abstract. Furthermore, the structure of the gem-diol in Figure 2 has been corrected (see figure below).

Comment: Page 3775 and Page 3793 (Figure 5)

The proposed products from the reactions of oxosuccinic acid (citrolylformic 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 were used (Guzman et al, 2006b).

Response: We agree that the proposed products from aldol condensation are not detectable in our experiments. However these products have been reported in significant amounts in other studies (e.g. as stated in Buldain et al., 1985) and must be considered potentially atmospherically relevant. We therefore prefer not to discard them, but in the text we do stress that in our experiments these compounds apparently are not produced in amounts significant enough to influence our measurements.

Comment: 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.

Response: The following changes have been made (page 3776, lines 5-7) Old version: "We have investigated the evaporation and cloud forming ability of a series of atmospherically relevant oxo-dicarboxylic acids: oxosuccinic acid, 2-oxoglutaric acid, 3-oxoglutaric acid and 4-oxopimelic acid."

C2828

New version: "We have investigated the evaporation and cloud forming ability of a series of oxo-dicarboxylic acids: oxosuccinic acid, 2-oxoglutaric acid, 3-oxoglutaric acid and 4-oxopimelic acid, all of which have been detected in the atmosphere or are considered surrogate standards for atmospherically relevant organic compounds."

Comment: 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.

Response: We do assume that both β -oxo-acids have decomposed in the atomizer bottle prior to experiments. However, it is very likely that decomposition with similar products will occur in aqueous solution droplets under atmospheric conditions. Since many of the proposed products, such as pyruvic acid, have been detected in atmospheric aerosols, our results are highly relevant to aerosol research. Therefore, data for the β -oxo-acids has not been removed from the paper.

Comment: 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.

Response: The error has been corrected in Table 1.

Comment: Page 3789

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

Response: The numbering of carbon atoms in Fig. 1 is not supposed to follow IUPAC standard. The purpose of the figure is to demonstrate that oxosuccinic acid has an oxo-group in the β -position, relative to one of the acid groups. In all the other compounds, the α -carbon is marked as "2", and the β -carbon as "3" and to maintain clarity and

C2829

consistency we have decided to keep this numbering. However, we have added text to the first paragraph of Section 2.1 to emphasize that oxosuccinic acid can be viewed as an α -oxo-acid as well as β -oxo-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. Oxo-succinic acid undergoes the reactions of a β -oxo-acid described below and is therefore characterized as such in the following."

Please also note the supplement to this comment:

<http://www.atmos-chem-phys-discuss.net/10/C2823/2010/acpd-10-C2823-2010-supplement.pdf>

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

C2830

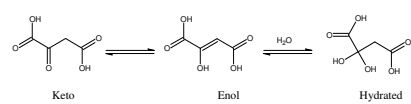


Fig. 1.

C2831