**Atmospheric
Chemistry
and Physics
Discussions**

Interactive
Comment

Interactive comment on "Evaluation of the atmospheric significance of multiphase reactions in atmospheric secondary organic aerosol formation" *by* A. Gelencsér and Z. Varga

Anonymous Referee #2

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The authors present an estimate of the importance of organic multiphase (i.e. aqueous phase) reactions for SOA mass formation. The subject is certainly appropriate for publication in ACP since to date the chemical/physical pathways which lead to organic aerosol mass formation are not yet well understood. The authors have chosen a simplified approach in order to derive a 'rule of thumb' what properties organic compounds should exhibit in order to act as efficient precursors for SOA formation in the aqueous phase (namely, $K_H > 1000$ M atm-1). The conclusions of their study provide some guidance for future laboratory, modeling and field activities which are focused on SOA sources. However, I feel that in some aspects this approach is oversimplified and the

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authors should discuss these aspects in order to show how robust their approach is or under what conditions the consideration of Henry's Law Constant KH might not be sufficient for the evaluation of the importance of an individual process.

General comments

- The authors assume a cloud life time of 1 h and thermodynamic equilibrium between the phases. However, it has been shown in several studies that achievement of thermodynamic equilibrium can take several minutes (if established at all) [e.g. Winiwarter et al., 1994, Audiffren et al., 1998] due to transport processes (e.g. diffusion in gas and/or aqueous phase, mass accommodation). The authors should at least mention that these delays might lead to smaller aqueous phase concentrations (and in turn, would require a higher KH).

- It should be pointed out that under certain conditions also low solubility species might contribute to mass formation. E.g., it is known that sulfate formation is dominated at high pH by the reaction of S(IV) and ozone though ozone has a Henry's Law Constant $<<$ 1 M atm-1).

Specific comments

p. 4412, l. 18/19: The treatment of the complete partitioning of oxalic acid into the particle phase is an overestimate of its particulate concentration. There are measurements that show that 20% (Baboukas et al., 2000) or 30% (Limbeck et al., 2005) of oxalic acid can be present in the gas phase.

p. 4412, l. 26: Clarify the difference between the present model approach and that one which has been applied by Ervens et al., 2004a: In the present model e.g. oxalic acid is not allowed to evaporate (l.18) and, thus, its concentration represents an upper limit of SOA mass. The same idea had been used by Ervens et al. 2004a who did not allow any evaporation of organics if the liquid water content falls below 1 mg kg-1, thus, 'trapping' all organics within the (aqueous) particle phase.

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p. 4414: I agree with Referee #1 that a conceptual figure describing the model would be helpful. This figure or some additional text should also clarify

- How is "cloud formation" (l. 10) treated? Does the liquid water content (LWC) increase slowly (i.e. is drop growth considered?) or is the LWC constantly 0.3 g m-3 for the full cloud period?

- is thermodynamic equilibrium always achieved between the phases or only at the beginning and end of the cloud cycle?

p. 4415, l. 17: How realistic is it to assume a yield of 100% for the oxidation steps in the aqueous phase?

p. 4415, l. 9: Define briefly "global reaction rate expression".

p. 4416, l. 19: "The model allows the calculation of the relative contributions of gas- and aqueous phase reactions over the entire process": A comparison of the yields from gas and aqueous phase processes would be useful. For such a comparison it should be noted that multiphase SOA formation is limited to only a couple of hours per day (= cloud life time).

p. 4416, l. 20: Clarify the sentence "Note that...". What is meant here?

p. 4419, l. 507: The oxidation of hydroxyacetone has been investigated by Stefan and Bolton, 1999.

p. 4419, l. 20: Is the Henry's Law Constant of methacrolein as quoted here the effective or physical Henry's Law constant?

p. 4420, l. 10-12: An additional aspect of the comparison between organic vs. S(IV) oxidation is the formation of 'small' high volatility products from organics (e.g. HCHO, CO2) which lead to smaller mass yields compared to S(IV) in which case all S(IV) is converted finally into sulfate mass.

Figure 1 and 2: Please give more details what assumptions you have made to convert

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the aerosol masses into % yield. A rough estimate I did myself yields a molecular weight of 100 g mol-1 for the organic product (which is not unreasonable but should be noted in the text or figure caption.)

Technical comments

p. 4411, l. 5: Correct the reference Jang and Kamens (2001) either here or in the reference list (Jang and Kamens (1999) is not quoted throughout the text).

p. 4420, l.. 4: replace "...while typical aqueous phase oxidation of SO2...are faster..." by "...typical aqueous phase oxidation rates of S(IV)...are higher ..." Figures 1 and 2: Check the units of the rate constants. Are they really meant to be second order or rather first order (i.e. s-1)?

References

- Audiffren, N., Renard, M., Buisson, E. and Chaumerliac, N., Deviations from the Henry's Law equilibrium during cloud events: a numerical approach of the mass transfer between phases and its specific numerical effects, Atmosph.. Res. 49, 139-161, 1998.

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- Limbeck, A., Y. Kraxner, and H. Puxbaum, Gas to particle distribution of low molecular weight dicarboxylic acids at two different sites in central Europe (Austria), J. Aeros. Science, 36, 991-1005, 2005.

- Stefan, M. I., and J. R. Bolton, Reinvestigation of the Acetone Degradation Mechanism in Dilute Aqueous Solution by the UV/H2O2 Process, Environ. Sci. technol. 33, 870-873, 1999.

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S., Schell, D., Kaminski, U., Pahl, S., Schneider, T., Berner, A., Solly, I. and Kruisz, C., 1994, Henry's Law and the Behavior of Weak Acids and Bases in Fog and Clouds, J. Atm. Chem. 19, 173-188.

Interactive comment on Atmos. Chem. Phys. Discuss., 5, 4407, 2005.

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