

## ***Interactive comment on “CLEPS: A new protocol for cloud aqueous phase oxidation of VOC mechanisms” by Camille Mouchel-Vallon et al.***

**Anonymous Referee #1**

Received and published: 21 October 2016

The authors present a ‘Cloud Explicit Physicochemical Scheme’ that describes the chemical processing of organic and inorganic compounds in the atmospheric aqueous phase of cloud droplets. This is a timely topic since for decades, atmospheric gas phase chemistry has been described in detail whereas chemical reactions in the aqueous phase have not gained as much attention due to the lack of data and its complexity that hampers a comprehensive inclusion in models. Special emphasis is given here to the treatment of organic compounds and a method is presented to estimate branching ratios of C2-C4 compounds and to track all their oxidation products. For about 15 years, another aqueous phase mechanism exist, CAPRAM (in various versions) that can be considered the ‘standard’ in atmospheric multiphase modeling. While the authors cite some of the papers of CAPRAM development and application, they fail to highlight the similarities of the mechanisms (it seems to me that the inorganic chem-

C1

istry has been completely taken from CAPRAM) and to discuss the consequences of the additions/changes. The modifications of the aqueous phase mechanism here are based on several assumptions – but so are also some of the parameters in CAPRAM. A discussion is missing of the extent to which the new assumptions are more reliable and necessary and therefore lead to a more consistent aqueous phase mechanism. In summary, in my opinion the manuscript lacks originality and novelty and fails to discuss uncertainties in the current mechanism and similarities/differences to previous work. I might recommend publication of this paper if the following comments are thoroughly addressed.

Main comments

### 1) Motivation of the current study

The intention of developing a ‘complete’ and ‘correct’ aqueous phase mechanism is clearly an ambitious and laudable project. However, it is clear that due to the lack of data many assumptions have to be made that should be better justified here. While such a mechanism can be used in a box model to assess chemical interactions in the multiphase system, it is impossible to track hundreds of species in a larger scale model. Therefore, I am missing a clearer direction on how this goal can be reached. For example, previous studies have suggested several strategies to reduce chemical mechanisms (Ervens et al., 2003; Ervens et al., 2008; Deguillaume et al., 2009; Woo and McNeill, 2015) for use in larger models. One way of reducing models is identifying the most important reactions and species. Such a discussion is missing here. – Instead as further directions it is suggested to include more species (succinic acid, tartronic acid).

### 2) Similarities to CAPRAM

a) In the abstract and also later, it is claimed that ‘a new detailed aqueous phase mechanism ... is proposed’. Given that all inorganic chemistry seems the same as other mechanisms (such as CAPRAM) and also all ‘overall’ rate constants are the

C2

same, I think this statement is highly exaggerated. I suggest marking in the reaction tables those processes and parameters that are new or different.

b) It seems to me that several simplifications that have been tested in CAPRAM (Ervens et al., 2003) are repeated here – without the previous detailed sensitivity studies. Such simplifications include skipping the formation of peroxy radicals as an individual step (p. 9, l. 1-5), the self-recombination of peroxy radicals (p. 9, l. 10) and skipping of the tetroxide (p. 9-10). The previous work should be properly referenced here.

c) How does the analysis of OH(aq) sinks and sources (p. 15, top) compare to previous studies such as CAPRAM (Herrmann et al., 2000; Ervens et al., 2003; Deguillaume et al., 2009; Tilgner et al., 2013)?

d) How does the modeled evolution of the O/C ratio compare to the trends as shown by (Schrödner et al., 2014)? Can the differences be ascribed to the more complex formulation of the branching ratios of the organic reactions?

### 3) Basis of assumptions

a) Assumptions on equilibria (hydration, dissociation, gas/aqueous partitioning)

In Sections 3.1, 3.2 and 5.2, it is explained how unknown equilibrium constants are estimated. While it is clearly necessary to estimate such parameters due to the lack of their availability, it should be shown (i) the validity of these assumptions, (ii) a comparison of the estimated parameters to (the few) known parameters and (iii) which assumptions have been made in other aqueous phase mechanisms and whether these assumptions are less appropriate.

b) I understand that a completely consistent coupling of MCM and the aqueous phase mechanism is difficult. However, the fact that numerous species do not have a gas or aqueous phase equivalent, respectively (p. 11, Section 5.1) introduces an unnecessary inconsistency. In my opinion, it would be more consistent to introduce a solubility threshold (Henry's law constant) that determines where a species should reside.

## C3

c) How well do calculated Henry's law constants based on GROMHE SAR compare to measured values? Can you refer to some comparison in a previous study or show it here (possibly in supplemental information)?

### 4) Inconsistencies in the presented mechanism

a) Dissociation equilibria

- In Eq. 4, the resulting  $K_A$  constant should be dimensionless. In the Equilibria table in the supplemental information, data are given in M (according to literature). The unit is missing in this table and therefore it is very confusing and leads to a bias of a factor 18 (molecular weight of water) in all dissociation constants. How have the numbers in the table been used in the model?

- Later in the manuscript (p. 12, l. 28), it is stated that the equilibria are split into forward and back reaction. What values are used? How were they derived?

b) Table 2 I do not understand the third example in Table 2. The 'global rate constant' is given as  $3.2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ ; however, all rate constants for the various branching pathways exceed this number and yield a value that is an order of magnitude greater. Is this just a typo or were these (and possibly other?) rate constants used like this used in the model?

### 5) Discussion of results

a) Length of cloud In several previous model studies, it has been discussed in detail that cloud processing time is on a time scale on the order of a few minutes or at most an hour as it is restricted by the lifetime of a droplet (e.g., Feingold and Kreidenweis, 2002; Ervens et al., 2004; Tilgner et al., 2013). Therefore, the conclusions of the aqueous phase on the oxidation capacity of the atmosphere should be revised and related to more atmospherically relevant conditions.

b) OH profiles Several previous studies have shown that the OH concentration in the gas phase is substantially reduced in the presence of clouds (Herrmann et al., 2000;

## C4

Ervens et al., 2003; Tilgner et al., 2013). The current mechanism shows a doubling of OH(gas) during cloud. Admittedly, the initial conditions were slightly different than in the CAPRAM simulations. However, given the robustness of the previous results for various scenarios, the differences of the current study to previous ones should be discussed.

c) How do the differences between the three scenarios in Fig. 3b compare to previous model studies? Can possible differences be ascribed to the new organic pathways?

6) Previous literature on aqueous phase chemistry

- p. 2, l. 12: In previous literature (Herrmann et al., 2015, and references therein) it is discussed that the presence of an aqueous phase (cloud) leads to the separation of the soluble HO<sub>2</sub> and the rather insoluble NO in the gas phase. Since their reaction is suppressed, less OH is formed. Therefore, it is not radical chemistry in the aqueous phase but different pathway strengths in the gas phase that lead to differences in OH during cloud.

- p. 2, l. 3: The statement that photolysis rates are 'highly enhanced in clouds' is not always true. While in thin clouds, photolysis rates are enhanced, in dense cloud they might be reduced (cf e.g. Fig. 2 in Ervens, 2015).

- p. 3, l. 5: In the cited paper (Ervens et al., 2015) it is discussed that oligomerization of MACR and MVK is rather unimportant in the atmosphere because of the low solubility of these precursors.

- p. 6, l. 30ff: How well does the product distribution estimated here matches the detailed laboratory study (Perri et al., 2009)?

- p. 8, Section 3.6: Results of a recent key paper on aqueous photolysis should be discussed here (Epstein et al., 2013).

- p. 8, l. 34-36: In the study by Ervens et al., 2015 it is stated "Unlike in laboratory experiments, atmospheric aqueous aerosol particles can be considered saturated with

C5

oxygen (~270 μM) due to their large surface–volume ratio. In all our model sensitivity studies with the multiphase model, the oxygen concentration reached saturation level after a few seconds." – which is not clearly reflected in the text in the current manuscript.

- p. 14, l. 37ff: A lower OH concentration will not only lead to lower formation rates of these acids but also to lower destruction rates (Ervens et al., 2014). Therefore the role of OH for the total organic acid levels depends on the ratio of k(formation)/k(destruction), which, in turn, might be a function of pH. This should be mentioned here.

Technical and minor comments

p. 5, l. 21: 'Rate constants'

p. 7, l. 24; p. 8, l. 14, and some other places in the manuscript: 'Reaction rates' are defined as the product of a rate constant and reactant concentration(s). It should be 'rate constant'.

p. 10, l. 28: Give a reference for this concentration.

p. 15, l. 26: Which acids are included in 'total acids'? Do they include formic and acetic acid?

Table 1: The references below the table should be added to the main reference list and not listed here.

Table 4: What parameter does the footnote (b) refer to?

Figure 2, caption: 'Relative' should be replaced by 'related'

Fig. 3 and 4: Add in the caption that the red line is hidden by the blue one or even choose different line types (e.g., dotted vs solid)

Fig. 5: Clarify the caption: '10 most important species' in terms of what?

C6

## References

- Dequillaume, L., Tilgner, A., Schrödner, R., Wolke, R., Chaumerliac, N., and Herrmann, H.: Towards an operational aqueous phase chemistry mechanism for regional chemistry-transport models: CAPRAM-RED and its application to the COSMO-MUSCAT model, *J. Atmos. Chem.*, 64, 1,1-35, 10.1007/s10874-010-9168-8, 2009.
- Epstein, S. A., Tapavicza, E., Furche, F., and Nizkorodov, S. A.: Direct photolysis of carbonyl compounds dissolved in cloud and fog droplets, *Atmos. Chem. Phys. Discuss.*, 13, 4,10905-10937, 10.5194/acpd-13-10905-2013, 2013.
- Ervens, B., Carlton, A. G., Turpin, B. J., Altieri, K. E., Kreidenweis, S. M., and Feingold, G.: Secondary organic aerosol yields from cloud-processing of isoprene oxidation products, *Geophys. Res. Lett.*, 35, 2,L02816, 10.1029/2007gl031828, 2008.
- Ervens, B., Feingold, G., Frost, G. J., and Kreidenweis, S. M.: A modeling study of aqueous production of dicarboxylic acids, 1. Chemical pathways and speciated organic mass production, *J. Geophys. Res. - Atmos.*, 109, D15,D15205, doi: 10.1029/2003JD004387, 2004.
- Ervens, B., George, C., Williams, J. E., Buxton, G. V., Salmon, G. A., Bydder, M., Wilkinson, F., Dentener, F., Mirabel, P., Wolke, R., and Herrmann, H.: CAPRAM2.4 (MODAC mechanism): An extended and condensed tropospheric aqueous phase mechanism and its application, *J. Geophys. Res.*, 108, D14,4426, doi: 10.1029/2002JD002202, 2003.
- Ervens, B., Renard, P., Tili, S., Ravier, S., Clément, J. L., and Monod, A.: Aqueous-phase oligomerization of methyl vinyl ketone through photooxidation – Part 2: Development of the chemical mechanism and atmospheric implications, *Atmos. Chem. Phys.*, 15, 16,9109-9127, 10.5194/acp-15-9109-2015, 2015.
- Ervens, B., Sorooshian, A., Lim, Y. B., and Turpin, B. J.: Key parameters controlling OH-initiated formation of secondary organic aerosol in the aqueous phase (aqSOA), *J.*

C7

- Geophys. Res. - Atmos.*, 119, 7,3997-4016, 10.1002/2013JD021021, 2014.
- Feingold, G., and Kreidenweis, S.: Cloud Processing of Aerosol as Simulated by a Large Eddy Simulation with Coupled Microphysics and Aqueous Chemistry, *J. Geophys. Res.*, 107, D23,doi: 10.1029/2002JD002054, 2002.
- Herrmann, H., Ervens, B., Jacobi, H.-W., Wolke, R., Nowacki, P., and Zellner, R.: CAPRAM2.3: A Chemical Aqueous Phase Radical Mechanism for Tropospheric Chemistry, *J. Atmos. Chem.*, 36,231-284, 2000.
- Herrmann, H., Schaefer, T., Tilgner, A., Styler, S. A., Weller, C., Teich, M., and Otto, T.: Tropospheric Aqueous-Phase Chemistry: Kinetics, Mechanisms, and Its Coupling to a Changing Gas Phase, *Chemical Reviews*, 115, 10,4259-4334, 10.1021/cr500447k, 2015.
- Perri, M. J., Seitzinger, S., and Turpin, B. J.: Secondary organic aerosol production from aqueous photooxidation of glycolaldehyde: Laboratory experiments, *Atmos. Environ.*, 43,1487-1497, 2009.
- Schrödner, R., Tilgner, A., Wolke, R., and Herrmann, H.: Modeling the multiphase processing of an urban and a rural air mass with COSMO–MUSCAT, *Urban Climate*, 10, Part 4, 0,720-731, <http://dx.doi.org/10.1016/j.uclim.2014.02.001>, 2014.
- Tilgner, A., Bräuer, P., Wolke, R., and Herrmann, H.: Modelling multiphase chemistry in deliquescent aerosols and clouds using CAPRAM3.0i, *J. Atmos. Chem.*, 70, 3,221-256, 10.1007/s10874-013-9267-4, 2013.
- Woo, J. L., and McNeill, V. F.: simpleGAMMA v1.0 – a reduced model of secondary organic aerosol formation in the aqueous aerosol phase (aaSOA), *Geosci. Model Dev.*, 8, 6,1821-1829, 10.5194/gmd-8-1821-2015, 2015.

Interactive comment on *Geosci. Model Dev. Discuss.*, doi:10.5194/gmd-2016-250, 2016.

C8