

Review of "Oxidation of low-molecular weight organic compounds in cloud droplets: development of the JAMOC chemical mechanism in CAABA/MECCA (version 4.5.0gmdd)
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The authors present a new chemical mechanism (JAMOC), implemented in MECCA. JAMOC includes explicit oxidation steps of organic compounds in the aqueous phase of cloud droplets and thus exceeds previous aqueous phase chemistry mechanisms suitable for box, regional and global modeling. Such extensions are urgently needed as currently, particularly in global models, aqueous phase chemistry modules are largely limited to sulfur(IV) oxidation.

However, the current manuscript needs major clarifications and additions to make it a comprehensive and useful extension to previous multiphase model studies. The choice of the newly added reactions is not always evident and also the discussion of the example results in Figure 3 is misleading. In addition, at several places, terminology is confusing or inaccurate. Also previous literature on atmospheric multiphase modeling should be properly discussed. Overall, while I think that this reaction mechanism could possibly become a useful addition to the currently used ones, my comments below need to be carefully addressed prior to possible recommendation for publication.

Major comments

1. Oligomerization has been discussed to be only relevant in the aqueous phase of aerosol particles where organic concentrations may be higher than in cloud droplets (Ervens et al., 2015; Perri et al., 2009; Tan et al., 2009). Thus, it is not clear why they are included in the mechanism. While aqueous phase reactions might also occur in the aqueous phase of aerosol particles, such an extension would also need to include adjustments of Henry's law constants and kinetic reaction rate constants for high ionic strength. Thus, this seems out of the scope of the current study.
2. The authors discuss at several places the role of gem-diols and the need of including their phase partitioning between gas and aqueous phases. Is there any indication of the relevance of such processes? Given the very small concentration of water in the gas phase, the stability of gem-diols in the gas phase is likely very small. I assume that their gas phase fraction is likely negligible. Unless the authors can provide literature or estimates on their Henry's law constants that show the opposite, I would not identify the inclusion of their partitioning into atmospheric chemical mechanisms as one of the main gaps in current mechanism developments. In fact, the hydrated glyoxylic acid has been shown to be of such low volatility that it can be involved in new particle formation (Liu et al., 2017)
 - Please show the estimated Henry's law constants in Table 1.
 - Add references that indicate their potential relevance in the gas phase.
3. At several places in the manuscript, it is not clear whether the authors refer to predictions of aqueous phase rates and budgets or to both phases. For example,
 - l. 59: R1 is certainly not a major sink in the atmosphere, but only in the aqueous phase
 - l. 190: is the explicit oxidation of OVOCs only added in the aqueous or also in the gas phase?
4. At several places in the manuscript, misleading or wrong terminology is used, e.g.
 - l. 38: 'nitrogen trioxide' is usually referred to as 'nitrate radical'
 - l. 50: 'simulating hydration and dehydration explicitly' implies that the hydration reaction and dehydration reactions are implemented. However, it seems that only the equilibria are included, separately from the gas/aqueous phase partitioning described by Henry's law.

- I. 134: Do you mean 'recombination of alkyl radicals', i.e. the self-reaction of two radicals?

5. The model studies are performed for a period of 5 days. However, the typical lifetime of a cloud droplet is on the order of 30 min or less (i.e. the time a droplet spends between cloud base and top in up- and downdraft regimes). You should at least mention that the model simulations are highly idealized and should be regarded as a sensitivity study rather than a realistic scenario.
6. The authors imply that the additional OVOC oxidation in the aqueous leads to the significant decrease in predicted OH concentration. However, the main reason why significantly less OH is observed in the presence of clouds is the decrease in its formation rate in the gas phase from the reaction of NO + HO₂. These reactants are separated due to their significantly different water-solubility, e.g. (Jacob, 1986; Lelieveld and Crutzen, 1990). Consequently, the lower HO₂ and higher NO levels in the presence of clouds are not due to the different water solubilities of OH and HO₂ but because of the differences in the gas phase photochemical cycles of HO_x and NO_x. This should be discussed and analyzed in Section 3.
7. Given that currently only a small fraction (~ 15%) of organics in cloud water can be identified on a molecular basis, (e.g., Herckes et al., 2013), implies that also even the most detailed chemical aqueous phase mechanism is likely largely incomplete in terms of organic species. Thus, also the predicted OH(aq) concentration is likely biased high as by far not all sinks are included. The idea of the general scavenging rate constant as suggested by Arakaki et (2008) is that it can be applied to parameterize the loss of OH(aq). Thus, it would seem a reasonable 'short-cut' to implement water-soluble organic carbon (WSOC) mass as an additional 'species' in the mechanism that reacts with OH(aq) to account for missing OH(aq) sources. As the products may be in many cases other WSOC compounds, this reaction could be implemented as $WSOC + OH \rightarrow WSOC + HO_2$ ($k = 3.8e8 \text{ M}^{-1} \text{ s}^{-1}$). How would the implementation of this reaction change the results in general, and in particular the OH(aq) level? Is it then in agreement with the ranges as suggested (Arakaki et al., 2013)?
8. Figures 1 and 2 need to be improved:
 - Captions: 'The chemical aqueous phase mechanism of glyoxal (oxalic acid)' is not very meaningful. At the minimum, specify that it is the oxidation (formation) pathways by chemical radical processes as represented in JAMOC.
 - Add the names of the species next to the structures in both figures.
 - Caption Figure 1: what do you mean by 'Glyaq donates all three species'?
 - Caption Figure 1: Are there any sources of aqueous phase glyoxal known at all?
 - in cloud water, glyoxal is predominantly present in its dihydrate form and should be represented as such in the figure. The mono hydrate may form if there is limited water available, and the unhydrated is likely not present at all (Ervens and Volkamer, 2010).
 - Figure 2: How is the phase partitioning of oxalic acid represented in JAMOC? Given that oxalate forms numerous salts and complexes in the condensed phase, the representation of the phase partitioning based on Henry's law is likely not appropriate.
 - Figure 2: Is the oxidation of oxalic acid by NO₃ ignored in the mechanism? If so, why?

9. Discussion and Figure 3: The extent is not clear to which the reduction of gas phase mixing ratios is due to uptake into the aqueous phase or due to chemical loss in either phase. I suggest showing total mixing ratios (i.e. gas + aqueous) which would give information on dissolution or net loss, respectively.

Minor comments

I. 17: 'liquid' should be replaced by 'aqueous'

I. 65: It is not clear which reaction is referred to here ('reaction with ozone with hydroxide'). Do you mean R2, i.e. the reaction of ozone with the superoxide anion radical (O₂⁻)?

I. 69: 'only outgassing depends on Henry's law constant' – I don't understand this. The standard equations used for the description of mass transfer, e.g. Eq-69 in (Sander, 1999), include the Henry's law constant which is needed to describe the deviation from equilibrium and thus the concentration gradient that drives the uptake or evaporation, respectively, of species.

I. 112: I disagree with the authors that 'little is known' about NO₃ reactions. There are quite extensive data sets available for NO₃ reactions with organic compounds in the aqueous phase, e.g., (Herrmann, 2003, 2015; Herrmann et al., 2010)

I. 127: Why was the rate constant of the dimers estimated as being twice as large as that of the monomer? Is there any reference for this?

According to the general kinetic theory, the number of collisions of molecules (which determines the rate constant) scales inversely proportional to molecular mass. Thus, the assumption of a higher rate constant for molecules with doubled mass seems counterintuitive. In addition, the rate constant will also depend on the number of available groups at which the radical attacks. However, since dimers (such as the glyoxal dimer, e.g. (Kua et al., 2008)) form cyclic structures, this trend does not justify a higher rate constant either.

I. 165: Several multiphase model studies have shown that the direct uptake from the gas phase, Fenton chemistry and H₂O₂ photolysis are the main OH(aq) sources in cloud droplets (Deguillaume et al., 2004; Ervens et al., 2003; Herrmann et al., 2005). Compared to these sources, what is the relative contribution of photolysis of organic compounds to OH sources in the aqueous phase?

I. 170: What refers the value 2.33 to? Do you mean 'enhanced compared to the gas phase photolysis rate'?

I. 183/184: Why is the relative humidity 70%? Shouldn't it be 100% in clouds?

I. 186: I think it should read 'a stable cloud droplet population'

I. 186: A liquid water content of $3 \times 10^{-1} \text{ g L}^{-1}$ does not seem an appropriate liquid water content as it would result in ~ 10000 droplets /cm³ (with diameter of 40 micrometers). Was indeed this LWC used in the model or is it a typo and should read 0.3 g/m³?

I. 222: 'reaction rates' should be 'rate constants' or 'rate coefficients'. A reaction rate is rate at which a concentration changes, i.e. $d[C]/dt = -k[C]$ whereas k is the rate constant and $[C]$ is the reactant concentration (Seinfeld and Pandis, 2006).

I. 228: I am confused by this terminology. JAMOC stands for 'Jülich Aqueous phase mechanism of organic compounds', i.e. it is a chemical mechanism which is usually just a list of reactions and their parameters. Such a mechanism can then be implemented into a model that simulates, e.g. the formation of clouds and processing of chemical species?

Thus, rain-out is a process in a model, in which JAMOC comprises one module. Please clarify what you mean by 'model' and 'mechanism', respectively.

Technical comments

I. 39: 'react' should be 'reacts'

I. 49: 'extend' should be 'extended'

I. 182: 'modells' should be 'models'