Summary

This paper introduces a new protocol for developing a detailed aqueous chemistry mechanism. It emphasizes oxidation by OH, NO_3, and other oxidants in low NO_x and dilute conditions, and does not include accretion processes. The detailed aqueous chemistry mechanism, coupled with the Master Chemical Mechanism (MCM v.3.3.1), is applied to an ideal cloud situation to examine the behavior of the chemistry.

This is an exciting, new advancement for our understanding of aqueous chemistry, especially for the oxidation of organic compounds dissolved in cloud water. The paper is fairly well written, although several spots need to be clarified. The paper can be improved by providing more information on the test case, giving more discussion on how the mechanism and results compare to previous studies (with and without detailed aqueous chemistry), and cleaning up the presentation of the paper. My suggestions of needed clarifications are given below.

Specific Comments

1. Page 6, line 25 and Table 2. It is not completely clear to me what criteria are used to proceed with the reduction scheme. For example, why is a branch with a 19% contribution to the reaction removed? Is it simply because the other 3 pathways represent >75% of the global reaction rate? It seems that pathways that comprise 10% or less of the reaction rate can be ignored without much impact on the overall reaction scheme. What kind of impact occurs when the pathway contribution is larger, such as the 19% for the third example in Table 2?
2. Section 5. How does the CLEPS mechanism compare to previous aqueous chemistry studies (e.g. CAPRAM)?
3. Page 13, line 10. While Rosenbrock solvers have become commonplace in chemistry transport models, other solver techniques also adequately solve the gas-aqueous chemistry mechanism (e.g., Ervens et al., 2003, JGR; Barth et al., 2003, JGR; McNeill et al., 2012, ES&T).
4. Page 13, line 12. Please restate the objective of section 6. The introduction says that "the box model is tested for an ideal cloud situation", which implies some kind of evaluation. However, there is no evaluation of the model results provided and there is only one instance of a comparison with previous modeling work (page 14, line 30).
5. As a follow up to the previous comment, please include more discussion in Section 6 of how the model results in this paper compare to previous ones, e.g. McNeill et al., 2012; Tilgner et al., 2013; Herrmann et al., 2005 – which can hopefully be directly compared due to their similarity of the test case conditions, and also Lelieveld and Crutzen, 1991; Jiang et al., 1997; Barth et al., 2003; Ervens et al., 2008, and Tilgner et al., 2010.
6. Section 6.1. More information about the case needs to be included. Specifically, the latitude, longitude, altitude, and size of the drops. Later in the discussion of the results, "sunset" is often used but what time is sunset?

7. Section 6. I realize that the test case is an example. However, air parcels do not spend 12 hours in a cloud. Vertical motions maintain a cloud by moving air above its lifting condensation level. Thus, air parcels are constantly being transported into the cloud region (and out), and residence times are on the order of 10 minutes to 60 minutes. I suggest adding a statement commenting on this caveat. It is important because the results from this test case show that after a few hours aqueous chemistry controls the concentration of a dissolved trace gas, but in reality that air parcel is not in the cloud after a few hours.
8. Page 14, line 1. The isoprene diurnal profile is not realistic. It is explained by the gas-phase chemistry. Another factor is that the isoprene emissions are constant with time, while in reality they vary diurnally. Please discuss this factor in the paper.
9. Page 14, lines 9-12. I agree with the explanation of the H_2O_2 time evolution. In addition, SO_2 concentrations must be depleted in order for H_2O_2 concentrations to increase. Otherwise H_2O_2 would continue to be consumed by SO_2. Further, it is worth noting the time scales with respect to how long an air parcel actually spends inside a cloud.
10. Page 15, lines 16-19. How long does it take for aqueous-phase glyoxal concentrations to change from being controlled by mass transfer to being controlled by aqueous chemistry? Should we expect to see this in observations of clouds in the atmosphere where the air parcel residence time in cloud may be shorter?
11. Page 15, lines 22-23. The comment about acetic and formic acid concentrations is interesting, but I did not see these values plotted. Could they be included in the figure (or at least report the concentrations)?
12. Page 15-16. I did not completely understand the importance of dissolved organic carbon (DOC) and its role in the aqueous chemistry. Could more background information be provided?
13. The supplementary material shows the pH values for the simulation. The pH seems to be quite low (3-3.5). Could the authors explain why such a low pH occurs? Are the results similar to previous simulations of this case?

<u>Technical Comments</u>

1. Page 1. line 20. → multiphase
2. Page 1, line 34. “GROMHE” is not defined. Is it needed in the abstract?
3. Page 1, line 38. → The photolysis rates in both phases ….
4. Page 1, line 39. The word “evaluate” is not what is done in the paper.
5. Page 2, line 33. Please quantify what is meant by “low-NO_x” and “dilute”.

6. Section 2. Please cite the supplementary material listing the chemical mechanism and chemical species. This supplementary material is a good resource for researchers.
7. Page 3, Line 6. Please quantify “significantly soluble and highly reactive”. For example, I would suggest saying that their Henry’s Law coefficient is greater than a specific value.
8. Page 3, line 28. Please add information on what kind of “data are available”. I assume that Henry’s Law coefficients and reaction rates are meant, but this needs to be clear.
9. Page 3, line 31. Define “GROMHE”.
10. Page 5, line 23. Could a couple of sentences be added to explain “global reaction rate constants”?
11. Page 6, line 22. → Such a large set of species
12. Page 6, line 23. It seems that this paragraph should be part of the previous paragraph.
13. Page 8, line 14. → Although these reaction rates
14. Page 9, line 19. Add that the process is explained below this paragraph.
15. Page 11, line 20. → The last reaction
16. Page 12, line 13. Lelieveld and Crutzen (1991) adopted an accommodation coefficient value of 0.05 for soluble gases in which the accommodation coefficient was not known. Perhaps this reference began this practice and should be cited.
17. Page 13, line 20. → simulation has been run for 31 days. What is the purpose of a 31-day gas chemistry spin up?
18. Page 14, line 2. A sentence should be added to say something about the isoprene products diurnal profiles.
19. Page 14, line 16. When is sunset?
20. Page 14, line 22. → is also responsible
21. Page 14, lines 23-27. I suggest discussing the “with DOC” results together with the last paragraph on the page. That is, organize the discussion of Figures 3 and 4 to present “without DOC” results first, and then discuss “with DOC” results presented in Figures 3 and 4.
22. Page 14, line 32. When is nighttime?
23. Page 15, line 7. → in terms of concentrations
24. Page 15, line 13. In SM6, it would be helpful to either put names with the chemical formulas, or organize the list by groups (alkanes, alkenes, etc.) as is done on the MCM web page.
25. Page 15, line 25. → acids as main contributors
26. Page 15, line 25. Since this topic sentence has been known for a while, it would be good to cite the appropriate reference, for example Chameides (1984) JGR.
27. Page 15, line 37. → 15 LT … 14 LT (local time)

28. Page 16, line 9. → protocol provides
29. Page 16, line 12. → introducing, for example, the
30. Page 16, line 13. Remove “compounds”
31. Page 16, line 17, → to impact the O/C ratio
32. Page 16, lines 33-37 may be better placed at line 21
33. Table 4. I did not see where the (b) footnote is cited. What does the “constant” refer to?
34. Figures: Could there be tick marks on every axis so that it is easy to locate where the time is for each concentration time evolution?
35. Figure 5: The legend connected with the bottom 2 panels is too small to read. It may not be needed if it is the same as the legend in the top 2 panels.