Interactive comment on “Unexpected high yields of carbonyl and peroxide products of aqueous isoprene ozonolysis and implications” by H. L. Wang et al.

General comments:
The paper concerns a very interesting and important subject, i.e. aqueous phase ozonolysis of isoprene and its comparisons with the corresponding gas phase reaction, and for this reason, it needs to be published. ACP is an appropriate journal for that. However, the way it is written makes this paper difficult to follow. The writing and the order in which the results are presented are very clumsy. There are many things that are not proven, the results are often stated rather than demonstrated and a lot of justifications are provided a posteriori, making the whole paper difficult to read. Generally, the paper lacks illustrations, some tables could easily be added (see specific comments), this would help to improve the lack of demonstration. The specific objectives of the paper are not clear, they need to be more focussed, and thus the title may be changed accordingly.

Specific comments:
- **Abstract**: specify if the yields are molar yields or carbon yields. The last sentence is not clear: why is the surface of plants mentioned here? Was it experienced? Why should the surface of plants form carbonyls and peroxides?
- **Introduction**: the last paragraph is not clear: are these the objectives? It looks like a small summary of the results rather than real objectives. The comparison between aqueous phase and gas phase mechanisms is very interesting, it could be one of the main objectives of the whole paper.
- **Experimental**:
  o Because isoprene is not very soluble in water, the solutions of liquid phase isoprene were prepared in acetonitrile, and then they were diluted into water. Therefore, in all experiments, the aqueous phase concentrations of acetonitrile were higher than that of isoprene. The authors should add a discussion on whether the high amounts of acetonitrile can induce artefacts on the studied reactivity. For example, the reactivity of Criegee biradicals towards water molecules to form organic acids can be slowed down by the presence of acetonitrile.
  o Specify what inorganic or organic salts / acids were used for the pH control (pH 7, 5.4 and 3): these species can also contribute to reactivity artefacts.
  o The method used to measure aqueous phase ozone concentrations can also measure ROOH concentrations: discuss this point when the analytical method is presented.
  o The authors mention that isoprene and ozone can be transferred to the gas phase in the head space of the reactor, and based on Henry’s Law equilibrium, they evaluate the corresponding losses to 10.7% and 8.6%. What about their reactivity in the gas phase? What is its influence? How can the products formed in the gas phase (they are highly water soluble) interfere with the studied aqueous phase reactivity?
  o Aqueous phase concentrations of isoprene were not measured?
- **Results and discussion**:
  o **3.1 Products and chemical stœchiometry**: this part is very badly organised:
- It is stated that MAC and MVK are 1st generation products, and MG a 2nd generation product, but these results (which are well known in the gas phase) are not proved by the experiments in the aqueous phase in the present paper. Either the authors should assume that the mechanism is the same as in the gas phase (but after that, it will be difficult to discuss the differences of mechanisms between the 2 phases!), either they need to demonstrate these results by adapted experiments: in the latter case, the authors need to show the reactants and products time profiles (and determine the corresponding yields) during the first 5 minutes of reaction. Because 5 minutes of reaction is very fast, the authors could do extra experiments with slow kinetics, by reducing the reactants initial concentrations for example.

- Page 6426: lines 1-15: this part is oddly written and very difficult to follow
- The absence of effect of temperature and pH on products yields should be demonstrated and discussed just after the demonstration of 1st and 2nd generation reaction products
- Page 6426: line 27: what is the “experimental error”? the authors should discuss its values in the experimental section
- The authors claim it without any demonstration: MG is a secondary reaction product. However, is it possible that small amounts of MG are directly formed from isoprene? This should be verified with specific experiments.
- The discussion on the molar yields of reaction products and its comparison with Chen et al. (2008) is interesting, but I would prefer to see the results in a comparative table rather than global reaction equations (1, 2, 3 and 4) which are not real chemical reactions!
- The last paragraph (Page 6428: line 12-14) is not clear

  o 3.2 Mechanism: this part is also very badly organised:
    - All the mechanism explanation (Page 6429: lines 1-14) is based on gas phase knowledge: this should be clearly told, and the adequation of this mechanism to the aqueous phase should be discussed based on previous works and experimental evidences.
    - Can the lack of peroxide formation be due to the reactivity of the Criegee biradicals with acetonitrile?
    - If the molar yields of MAC and MVK formation in isoprene + OH reactions were 11 and 24%, that means that, compared to the isoprene + O₃ reaction studied here (where they are 42.8 and 57.7, respectively), they are smaller but not negligible. Therefore, it is not possible to state that OH radical formation was negligible in the present study (page 6430, line 1).

  o 3.3 A comparison between aqueous and gas phase reactions: this part is also very badly organised:
    - Page 6430: lines 15-16: what does mean “virtually identical on both reactants and products”?
    - Page 6431: lines 15-16: why are the peroxides yields (~68%) considered here “unexpectedly high”? Isn’t it contradictory with their “expected yield of 100%” in page 6429 (line 21)?
- **Conclusions and implications:**
  
  o Page 6434 line 3: add “our results suggested that compared to the corresponding gas phase reactions, condensed water could…”

**Minor comments:**

- Avoid all “of note” and “notably”: they are too many of them, and they not always used in the proper way, and they make the writing very heavy.
- Page 6426: line 11. A point was forgotten
- Page 6427: line 14: replace pyrovic by pyruvic
- Fig 1: the legend is not clear
- Table 1: H2O2 should be on the last column, and the total C yield should correspond to the column of organic reaction products. There should be a solid horizontal line between “Mean” and “total C”
- Page 6427, line 16, and Page 6434, line 1: for the total C yield, the authors should provide the same numbers as in table 1
- Page 6430, lines 8-9: the authors should provide the same numbers as in table 1
- Page 6429: line 14: replace Moortgata by Moortgat
- Page 6432: line 18: replace “acid” by “acids” and “is” by “are”
- Page 6433, last line : add *instrumental* detection limit