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Atmospheric Chemistry and Physics Discussions

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

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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.

Thanks for your constructive comments and suggestions. We have improved the writing and provided more illustrations in the revised manuscript. Here are our responses to your specific comments.

(1) 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?

A: All the yields are on the molar base. We specified this in page 6420 line 10-11in the manuscript. We have rewritten the related sentences to make the meaning more clearly in the revised manuscript.

(2) 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.

A: You are right. We have adjusted the last paragraph in the revised edition.

(3) Experimental: 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.

A: Your concern is important. So, we have added a experiment for aqueous isoprene ozonolysis in absence of acetonitrile to determine if acetonitrile could affect the products formation and the kinetics. 1-uL pure isoprene was injected directly into the 500-ml ozone solution in the reactor by a syringe and a sealed teflon stopple, and immediately the reactor was shaken for 2 min. The subsequent experimental steps are the same as those in the reaction system in the presence of acetonitrile. Under the conditions of pH=7, and T=4 °C or 10 °C , it turns out that the molar yields of MAC (48.1% at 4 °C ; 50.8% at 10 °C), MVK (58.1% at 4 °C; 60.2% at 10 °C), HMHP (18.2% at 4 °C; 16.8% at 10 °C), and hydrogen peroxide (59.1% at 4 °C; 60.0% at 10 °C) are near to those in the corresponding experiments in the presence of acetonitrile, with a relative deviation of less than 10%. Moreover, no organic acids were detected. In addition, Gäb et al. (1995) also indicated that acetonitrile would not affect the product distributions in the aqueous ozonolysis of alkenes, only slowed the ozonolysis rate, although the acetonitrile concentration used in their work was higher than ours. In summary, we thought 1% acetonitrile used in the present study has little effect on the products formation.

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.

A: We used H_2SO_4 to adjust the inital pHs. We found that the pHs didn't change during the investigated reaction time and the product yields were independent on the concentrations of H_2SO_4. Thus, we think that the observed products were not significantly affected by the added H_2SO_4.

The method used to measure aqueous phase ozone concentrations can also measure ROOH concentrations: discuss this point when the analytical method is presented.

A: Indigo disulphonate spectrophotometry was used to measure aqueous phase ozone concentration. We found that H_2O_2 couldn't react with indigo disulphonate. Peroxide compounds (ROOH) were analyzed by online HPLC, and the detailed information can be seen in the text. Thus we think that ROOH interference is negligeable for ozone measurement.

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?

A: We thought that 8.6% estimated by Henry's Law equilibrium was an upper limit for the aqueous isoprene loss to the gas phase, because acetonitrile could assist isoprene to dissolve in water and ozonolysis occurred immediately in the aqueous phase. The combined yield (CY) of MAC and MVK formed in isoprene ozonolysis was determined to be 50% in the gas phase (references therein the text) and 100% (42.8% MAC, and 57.7% MVK) in the aqueous phase (the present study) respectively. Assuming that the isoprene reacted with 5% in the gas phase and 95% in the aqueous phase, we should obtain a 97.5% CY; however, we observed a 100% CY. So we think that the gas phase isoprene reaction is minor (less than 5%) in our experiments.

Aqueous phase concentrations of isoprene were not measured?

A: Unfortunately, we didn't measure the aqueous phase concentration of isoprene because of the technique limitation. We estimated the aqueous concentration based on the assumption that the quantitively introduced isoprene was completely dispersed in the aqueous phase.

(4) Results and discussion: 3.1 Products and chemical stoechiometry: 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.

A: We mentioned in the manuscript that “MG was not observed when the isoprene was in large excess to ozone (e.g., C_{ISO}: C_{O3} >10:1)” (page 6425: lines 21-22). So we thought MG couldn’t be a first-generation production. And because “a minor amount of methylglyoxal (MG) was observed when C_{ISO}: C_{O3} =2 : 1”(page 6425: lines 19-20). We think MG is a 2nd generation product. MG is considered to be formed by the ozonolysis of MAC and MVK, which are first-generation products in the aqueous isoprene$-$$O_3$ reaction system.

Thanks for your suggestions about the reducing reactants initial concentrations. We have tried to do so, unfortunately found that the reaction lifetime was less than 1 second according to the kinetics. If the reatants concentration was decreased to one-hundredth, the products could not be detected by our instrument. Moreover, the longer the reaction lasted, the larger the uncertainty was for the measurement of unstable peroxides.

Page 6426: lines 1-15: this part is oddly written and very difficult to follow

A: We have rewritten this part, please see the revised manuscript.

The absence of effect of temperature and pH on products yields should be demonstrated and discussed just after the demonstration of 1^{st} and 2^{nd} generation reaction products

A: We have adjusted this part in the revised manuscript.

Page 6426: line 27: what is the “experimental error”? the authors should discuss its values in the experimental section

A: The experimental error is 2 standard deviation of the yields based on the 8 repeated experiments at certain pH and temperature.

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.

A: Please see the previous explanation.

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!

A: Here, we would like to make a combination between the work of Chen et al. (2008) and the present work, not a comparison. Such a combination was used to obtain the aqueous stoichiometric of isoprene and ozone when ozone was in excess. The work of Chen et al. (2008) reported the aqueous stoichiometric of MAC (MVK) and ozone. The present work focused on the question that how MAC and MVK came from isoprene in the aqueous phase, so the experiments were performed under the conditions that isoprene was in excess. This combination provides us a profile of the aqueous isoprene evaluation in the ozone excess, which is similar to the real atmosphere.

The last paragraph (Page 6428: line 12-14) is not clear

A: We have adjusted this paragraph in the revised manuscript.

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.

A: We would like to show that this aqueous phase mechanism was based on the present experimental results and the available corresponding gas phase mechanism, see page 6428: line 16-17 in the manuscript. We have added more discussion about the aqueous phase mechanism and a gas phase mechanism (Fig. 3a) as a comparison in the revised manuscript.

Can the lack of peroxide formation be due to the reactivity of the Criegee biradicals with acetonitrile?

A: Our additional experiment shows that the acetonitrile has not obvious influence on the peroxide formation. Please see the previous description.

If the molar yields of MAC and MVK formation in isoprene + OH reactions were 11 and 24%, that means that, compared to the isoprene + O_3 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).

A: We have known that the combined yield (CY) of MAC and MVK was 35% in aqueous isoprene-OH reaction (Huang et al., 2011) and 100% in the aqueous ozonolysis of isoprene (the present study) respectively. If the isoprene consumption was due to 5% by OH and 95% by O3, the CY was estimated to be 96.8%. The observed CY (100%) indicated that the isoprene-OH reaction was minor (less than 5%) in our experiments.

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"?

A: We mean that solvent effect on both reactants and products is energetically identical. We have revised this.

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)?

A: This "unexpectedly high" yield of peroxides in the aqueous phase was compared with that in the corresponding gas phase for which several studies reported up to date. Certainly, this yield is lower than the expected 100% yield deduced in the aqueous

mechanism, implying that other reactive oxygenated substances (ROS) possibly form in the reaction. In Fig.3b, we used "O" to represent ROS.

Page 6431: lines 15-30: a table including 1 column for gas phase findings and 1 column for aqueous phase findings should be added to illustrate the text, and help understanding the interpretations.

A: Thanks for your suggestion. We have added a comparison table in the revised manuscript.

Page 6432: lines 1-9: Do the authors suggest that the yields depend on the initial concentrations of isoprene?

A: The peroxide yield should be independent on the initial isoprene concentration. So we have deleted the related sentences.

Page 6432: lines 10-15: it is true that isoprene ozonides should encounter more H_2O molecules in the liquid phase than in the humid air, but under the present experimental conditions, it should also encounter a lot of acetonitrile molecules. This should be discussed.

A: Yes, we have discussed this in the revised manuscript. 1% acetonitrile seems to have unobvious effect on the products formation as mentioned above.

Reactions P1 and P2 should be more detailed with more references. In Reaction P1, the second part is probably an equilibrium. This needs further literature research.

A: Yes, we have added more references in the revised manuscript. The second part of P1 as an equilibrium was reported.

(5) Conclusions and implications: Page 6434 line 3: add "our results suggested that compared to the corresponding gas phase reactions, condensed water could…"

We have added this sentence.

(6) 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: H_2O_2 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

A: You are right. We have revised all the errors and shortcomings you pointed out.

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 6419, 2012.