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Atmospheric Chemistry and Physics Discussions

Interactive comment on "In-cloud processes of methacrolein under simulated conditions – Part 1: Aqueous phase photooxidation" *by* Y. Liu et al.

Anonymous Referee #2

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This manuscript reports a thorough product study for the OH-initiated oxidation of methacrolein in aqueous solutions representative of cloud droplets. A variety of analytical techniques was employed, and 25-57% of the carbon was accounted for. In addition, one kinetic measurement was made at 6 deg C, showing a similar rate coefficient to the 20 deg C value currently available. The data analysis appears thorough, but there are a couple of places where an improved/expanded discussion would allow the reader to be more thoroughly informed and educated. This manuscript is appropriate for publication in ACP after several improvements and corrections are made. It will be a valuable addition to the growing body of knowledge of aqueous phase processing of VOCs.

Major comments:

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1) I disagree with the authors' assertion that the kinetic study shows the nature of the chemical mechanism. I will accept that the measured rate coefficient is consistent with attack on the double bond, as shown by comparison to crotonaldehyde, acrolein, and C2-C5 saturated aldehydes. But kinetics studies do not "show" the mechanism to be OH-addition at the C=C bond and should not be interpreted so dramatically. (These statements occur in the abstract, in section 3.1, and in the conclusion.)

2) Why were kinetic measurements not made at 20 deg C for comparison with the results of Buxton et al.? Also, was the pH controlled in the kinetics experiments? If not, what was the likely change in pH over the course of the experiments?

3) The discussion of Figure 2 is inadequate. a) Section 3.2, lines 24-25: This sentence is overly general and not useful. Are you trying to tell me to compare data points of different colors for particular species? Which ones? Please be more specific. b) In what way does Figure 2 "show" that methylglyoxal etc. are primary reaction products? What feature of the data makes it "clear" ? You must explain your logic to the reader. c) Likewise, why does the data "show" that the minor products are secondary? You must explain the observation and how your chemical knowledge leads you to interpret the data with the conclusion that certain products are secondary. d) The figure caption should be more explanatory.

4) Section 4.2: The phrase "total carbon yield" needs an explanation of what you mean by this phrase, as differentiated from "molar yield". Presumably it is determined based on the branching ratio and the number of carbon atoms in the product, but please define.

Minor comments:

1) Figure 2 is much too small and too crowded to read. Please break it up into larger figures with less information in each panel.

2) Is it possible to make Figure 6 larger? It is difficult to read at its current size.

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3) What is the meaning of the word "efficient" in line 18 of the introduction? It is not clear in this context what point the authors are trying to make. Is there some less-efficient medium to which water is being compared?

4) The structures in Figure 3a look distorted and mis-aligned.

5) Section 2, line 8, "which was controlled through a specific experiment": this phrase does not explain what the authors did. What sort of experiment? what sort of control?

6) Section 2.3: what was the eluent profile for minutes 26-44? minutes 46-49? And if 60:40 was used for minutes 50-59, "during" should be replaced by "for"

7) pg 6402, line 7: please define "highly precise"

8) What is the uncertainty associated with using standards of similar, but different, compounds for ESI? Of particular interest is the peroxy compounds, which is quantified by comparison to a non-peroxy compound. How much might this influence your quantification of yields and branching?

9) Figure 6 should come before Figure 5 (and be renumbered as Figure 5) and should be called out the first time it is mentioned, which I believe is on pg 6405, line 15.

10) p 6405, line 18: what is a "formic aqueous solution"?

11) 4.1: please give the URL for the on-line calculator.

12) p 6409, line 4-5: the meaning of this sentence is not clear. Please elaborate.

13) It would be interesting to compare the branching ratios observed in the aqueous phase to those known for the gas phase oxidation of methacrolein via OH.

14) Table 2: are the values reported here the means of all the replicates of a particular experiment type?

15) F4 caption: "DHMP was most probably identified" – do you mean "was identified as the most probable product"?

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Grammar Corrections: 1) Introduction, lines 14 & 15, change "on" to "in" 2) p 6399 line 10: "highly emitted" is awkward phrasing. 3) Section 2, line 3: should be "described in detail in" 4) line 5: "which has an irradiance spectrum comparable to" 5) pg. 6402, line 2: "at a flow rate" 6) line 6: "to prevent contamination" 7) line 14" "used as the collision" 8) line 15: "at a pressure" 9) line 24: "standards whose chemical" 10) pg 6404, line 21: "either... or", not "either....either" 11) pg 6405, lines 5-6: "either... or", not "either....either" 12) line 6: "observed in" 13) line 12" "protocol" 14) Section 4.1, line 3, "As with most short" 15) line 14: "which prevents hydration" 16) pg 6407, line 1: "associated with it" 17) line 14" "UV-visible radiation" 18) pg 6408, line 24: "except formate" 19) pg 6409, line 13: there is no Figure 8. 20) line 14: do you mean "reacts with non-hydrated..."? 21) line 19: "methacrylic acid, whose structure is very" 22) line 24: "Figure 6 explains the formation" 23) line 27: "product, as observed" 24) pg 6410, line 2, remove the i.e., because you are speaking about only one particular product; it is not merely an example of a broad class of reaction products. 25) pg 6411, line 4: "the formation of" 26) T2 caption: don't leave the superscript "b" orphaned on a line like it currently is. 27) F3 caption: lower-case e on energy; "consisted of mixing"; "acetic acid for 10 days" 28) F4 caption: lower-case e on energy; "intensities' yields" is an unusual phrase. Is there some other way of describing what you mean?

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 6397, 2009.