

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

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The authors thank referee #2 for the interesting questions and comments raised, and also for the corrections. Answers to the questions are given below.

Major comments:

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.)

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We agree with referee #2, and this will be taken into account in the corrected manuscript. However, we want to insert some important additional information and discussion:

- a comparison with the study by Szeremeta et al. (2009), which was officially published after the submission of our manuscript to ACPD (see below).
- a determination of the free Gibbs energy derived from the Arrhenius parameters obtained from the data base constituted by the studies of Szeremeta et al. (2009), Buxton et al. (2000) and the current study (see below).
- a discussion on the obtained results (see answers to major comment 2, below)

2) Why were kinetic measurements not made at 20 °C for comparison with the results of Buxton et al.?

We performed our kinetic study at 6°C, which is more representative of in-cloud liquid water conditions than 20°C. This kinetic rate constant was experimentally investigated as a function of temperature by Szeremeta et al. (2009). The latter study was officially published after the submission of our manuscript to ACPD. Figure 1 shows the comparison between our rate constant value and those by Szeremeta et al. (2009) and Buxton et al. (2000). This Figure shows a very good agreement between the 3 studies.

We used this set of 7 concordant experimental values to determine the Arrhenius parameters :

$$\ln(k(T)) = \ln A - \frac{Ea}{RT} \quad (1)$$

Where:

$$\ln A = 27.8 \pm 0.71 \text{ M}^{-1} \text{ S}^{-1}$$

$$Ea = 12.1 \pm 1.73 \text{ kJmol}^{-1}$$

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The height of the energy barrier of the OH-oxidation of methacrolein reaction, expressed by the free Gibbs energy of activation ΔG^\ddagger can be calculated using the Gibbs–Helmoltz equation (2):

$$\Delta G^\ddagger = \Delta H^\ddagger - T.\Delta S^\ddagger \quad (2)$$

Where ΔH^\ddagger and ΔS^\ddagger are the activation enthalpy and the activation entropy, respectively, which can be expressed as a function of the Arrhenius parameters (equations 3 and 4) (Robson M, 2004):

$$\Delta S^\ddagger = R.[\ln A - \ln(\frac{k_B.T}{h}) - 1] \quad (3)$$

Where:

k_B = Boltzmann constant ($1.3806 \times 10^{-23} JK^{-1}$),

h = Planck constant ($6.6262 \times 10^{-34} Js$).

$$\Delta H^\ddagger = E_a - RT \quad (4)$$

At $T = 298$ K, we obtained:

$$\Delta H^\ddagger = 9.6 \pm 1.7 \text{ kJ.mol}^{-1}, \Delta S^\ddagger = 22.1 \pm 5.9 \text{ J.K}^{-1}.\text{mol}^{-1}, \Delta G^\ddagger = 16 \pm 3 \text{ kJ.mol}^{-1}$$

The obtained value for ΔG^\ddagger for OH-oxidation of methacrolein is slightly lower than the values obtained by previous studies for saturated compounds (Table 1), which undergo H-abstraction by OH radicals. This result may provide further evidence for another mechanism of OH-oxidation of methacrolein, faster than the H-abstraction.

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		ΔG^\ddagger values (kJ.mol ⁻¹)			reference
Number of saturated / unsaturated compounds	Mean value	min	max		
8 saturated	21 ± 5	19 ± 3 (1-propanol)	26 ± 8 (acetone)	monod et al., 2005	
5 saturated	22 ± 10	19 ± 10 (isobutyraldehyde)	25 ± 7 (diacetyl)	Gligorovski and Herrmann, 2004	
16 saturated	24	19 ± 5 (glyoxal)	30 ± 17 (malonate)	Ervens et al., 2003	
1 unsaturated		16 ± 3 (methacrolein)		This work	

Table 1: Free Gibbs energy of activation of aqueous phase OH-oxidation of saturated compounds compared to that of methacrolein.

This additional information and discussion will be added in the corrected manuscript.

2) (Continued) Also, was the pH controlled in the kinetics experiments? If not, what was the likely change in pH over the course of the experiments?

The kinetic experiments were performed at “free pH”, as in the reaction products 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.

The sentence “These figures show that an excellent agreement was obtained between experiments performed in the same conditions” will be replaced by “Figures 2a and 2b show that an excellent agreement was obtained between experiments performed in the same conditions: figure 2a shows an excellent agreement between experiments h (grey) and l (white) for the time profiles of methacrolein, acetate/acetic acid, hydroxyacetone, methacrylate/methacrylic acid, and glyoxylate, and figure 2b shows an excellent agreement between experiments a (blue), b (red) and c (green) for the yields of methylglyoxal and formaldehyde, and between experiments h (grey) and l (white) for the yields of oxalate and pyruvate”

3.b) In what way does Figure 2 “show” that methylglyoxal etc. are primary reaction

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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.

The primary reaction products are the first generation molecular products that are formed directly without other intermediate molecular reaction products. For these primary reaction products, the plot of their concentration as a function of consumed methacrolein is linear. Where the concentration of consumed methacrolein is given by:

$$\Delta[\text{methacrolein}] = [\text{methacrolein}]_0 - [\text{methacrolein}]_t$$

This is illustrated in figure 2 (left), with the example of methylglyoxal and formaldehyde, and also in Figure 3C for PMA, and in Figure 4C for DHMP. The secondary reaction products are the second generation molecular products that are formed through the reaction of primary reaction products. For these secondary reaction products, the plot of their concentration as a function of consumed methacrolein shows a horizontal tangent at the origin, and then an exponential behavior. This is illustrated in figure 2b (right), with the example of oxalate and pyruvate, and also in Figure 4C for DHMA. According to this method, we also determined that:

- acetate/acetic acid and hydroxyacetone were primary reaction products.
- methacrylate/methacrylic acid showed a double behavior: it was both a primary and a secondary reaction product: at the beginning of the reaction, the plot of its concentration as a function of consumed methacrolein is linear, but after 300 min of reaction, this plot shows a behavior of a secondary reaction product (exponential behavior).
- glyoxylate was a secondary reaction product.

Most of the time, the major reaction products are primary reaction products, but this is not always the case: for example, the primary reaction products derived from the OH-

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oxidation through H-abstraction on the CH₃ group of methacrolein was not detected, thus showing this pathway was of minor importance.

The manuscript will be changed accordingly.

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.

For the primary reaction products, the plot of their concentration as a function of $\Delta[\text{methacrolein}]$ is a linear regression, and its slope represents their molar yield. For example, the average molar yields of methylglyoxal and formaldehyde for experiments a, b and c are 6% and 10.2% respectively (see Figure 2).

For each primary reaction product, the carbon yield is determined from its molar yield, by equation (5):

$$\text{carbon yield} = \frac{\text{carbon number}_{(\text{product})}}{\text{carbon number}_{(\text{MACR})}} \cdot \text{molar yield}_{(\text{product})} \quad (5)$$

Finally, the total carbon yield was calculated from the sum of the carbon yields of each quantified primary reaction products.

Minor comments:

1) and 2) The information reported in these figures need to stand on one single figure. We will enlarge that figure, but we do not want to break it into several figures.

4), 9) and 15) will be corrected in the manuscript.

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?

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The word "efficient" refers to the findings of Monod et al., (2005) who showed that in-cloud photooxidation of all the studied VOCs is faster than the same reactions in the gas phase.

The reference to Monod et al., (2005) will be added to that sentence in the corrected manuscript.

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?

We performed two specific experiments: a) One experiment of direct photolysis of methacrolein (with no H₂O₂, and initial concentration of methacrolein = 4.0.10⁻³M), and we found no significant decrease of methacrolein after 29h of photolysis. b) Another experiment of reaction of methacrolein (initial concentration = 4.0.10⁻³M) towards H₂O₂ (initial concentration = 0.4M) in the dark during 24h has shown that the reaction of methacrolein towards H₂O₂ was of negligible importance compared to OH-oxidation, under our experimental conditions. These precisions will be added in the manuscript.

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"

The sentence "A binary eluent (H₂O : CH₃CN) was used at 1 mL.min⁻¹, with H₂O : CH₃CN: 60%:40% from 0 to 25min; 0%:100% at 45min; 60%:40% at 50min during 10min" will be replaced by "A binary eluent (H₂O : CH₃CN) was used at 1 mL.min⁻¹, with H₂O : CH₃CN = 60%:40% for 25min, evolved to 0%:100% from 25 min to 45min, then evolved to 60%:40% from 45 to 50min, and then lasted isocratic for 10min"

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

Experiments h and i were performed by directly coupling the aqueous phase photoreactor with the ESI-MS-MS. A continuous flow of the solution was directly injected by infusion into the MS, and measured continuously during the reaction (about 20 hours)

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by MS in the positive and the negative modes, with 10 minutes alternative between the two modes. This procedure permitted to avoid all the problems inherent to sampling, and sample storage, and thus to obtain much more precise time profiles for each reactant or reaction product.

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?

It is difficult to associate an uncertainty using standards of similar but different compounds for ESI. For most of the not commercially available compounds, we used standards with the same chemical structure except for a methyl group, and assumed the analytical uncertainty was the same.

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

This expression will be changed to "aqueous solution acidified with formic acid" in the corrected manuscript.

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

Please find below the URL for the SPARC online calculator

<http://ibmlc2.chem.uga.edu/sparc/>

This will be added in the corrected manuscript.

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

See explanations in the answer to major comment 3.b) and c).

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.

This is a very interesting suggestion. According to our study, the attack of OH on

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methacrolein occurs only about 5% via abstraction of the carbonyl hydrogen in the aqueous phase. In the gas phase, Pimentel and Arbilla, (1999) and Orlando et al. (1999), the branching ratio of this pathway is 45% and 50% respectively. Concerning the reaction products, the aqueous phase OH-oxidation of methacrolein produces formaldehyde, methylglyoxal, hydroxyacetone, carboxylic acids and larger molecular weight compounds and oligomers. In the gas phase, the reaction products (which account for more than 90% of the reacted carbon) observed by Orlando et al., (1999) were CO, CO₂, hydroxyacetone, formaldehyde, and methacryloylperoxynitrate (MPAN). These differences show that the reaction mechanism in the aqueous phase is quite different from the one in the gas phase. The presence of nitrate compounds in the gas phase (MPAN) is due to the presence of NO_x in the mixture. Because NO_x are very low soluble, they are not considered in the aqueous phase. We did not analyze the amount of CO and CO₂ formed during the course of the reaction. However, this comparison seems to show that the aqueous-phase reactions enable the formation of new structures where the initial C-C bond structure is more preserved than the corresponding reactions in the gas phase. This will be added in the corrected manuscript.

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

Yes, the values reported for Exp. A are the means of experiments a, b and c, and the values reported for Exp. B are the means of experiments d, e, f, g, h and i. This will be added in the legend.

Grammar Corrections:

Corrections 1), and 3-27) will be changed in the corrected manuscript

2) p 6399 line 10: "highly emitted" is awkward phrasing.

The sentence "These sources make methacrolein a high emitted compound in the atmosphere, with a global emission rate higher than 100 Tg/y" will be changed to

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"Methacrolein is largely emitted in the atmosphere, with a global emission rate higher than 100 Tg/y"

28) F4 caption: lower-case e on energy; "intensities' yields" is an unusual phrase. Is there some other way of describing what you mean?

"intensities' yields" will be replaced by "Intensities as a function of consumed methacrolein"

References

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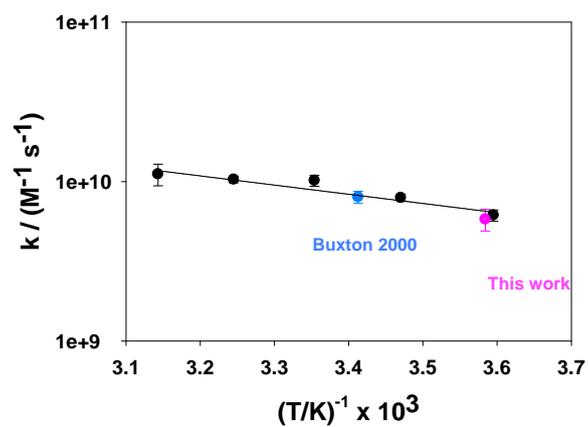


Figure.1 : Rate constants of OH-oxidation of methacrolein as a function of temperature: comparison between the values obtained by Szeremeta et al., (2009) at pH = 7 (black), Buxton et al. (2000) at pH = 4 (blue) and this work at « free pH » (pink).

Fig. 1.

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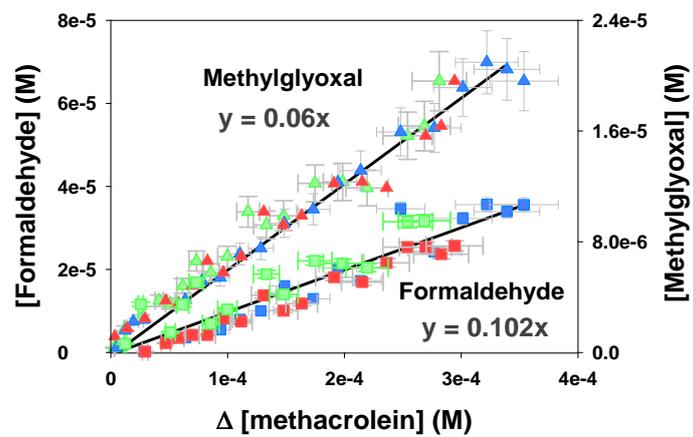


Figure 2: Example of molar yield determination of methylglyoxal and formaldehyde for experiments a (blue), b (red) and c (green).

Fig. 2.

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