

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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We thank anonymous referee #1 for constructive comments and issues raised by the review. They will be taken into account in the corrected manuscript. The authors wish to answer, below, to the interrogations/comments of anonymous referee #1.

General comments: *Liu et al. studied the photochemical reactions of methacrolein, which can be derived from oxidation reaction of isoprene and direct anthropogenic emission in the atmosphere. In their manuscript, main result is that they determined bimolecular rate constant for methacrolein with OH radical and identified some of the reaction products under simulated cloud conditions. The objectives and study itself are quite interesting, however, the conditions of cloud (as shown in their title) need to be better simulated, and especially pH often significantly affects the reaction rates. Thus,*

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the reviewer recommends that this report needs a significant change, and hopes to see more experimental data, especially the effects of pH on bimolecular rate constants so that the information the authors provide will be a merit for the readers of Atmospheric Chemistry and Physics.

Methacrolein comes from mainly the oxidation of isoprene which is the most abundant biogenic compound with a global emission of 500-750Tg/yr. Its presence in aqueous phase of cloud has been observed above forested area, where the pH of cloud's liquid droplets is close to the pH of clean tropospheric clouds (~5.6). Therefore, our aqueous phase photooxidation of methacrolein experiments were carried out at “free pH”, which corresponds to these conditions. The main objectives of the study were to identify and quantify the reaction products, to establish the reaction mechanism of OH-oxidation of methacrolein, and to estimate the carbon yield.

Additionally, we studied the kinetic rate constant of OH-oxidation of methacrolein at 6°C. Under atmospheric conditions, it is known that the pH value influences the kinetics of bimolecular reactions when at least one of the two reactants is a weak acid, with a pKa value of the order of the pH encountered in the atmosphere. Here, this is not the case since both methacrolein (pKa > 14) and OH radicals (pKa = 12) have pKa much higher than the range of pH encountered in the atmosphere (roughly from 2 to 7.5). Additionally, the kinetic rate constants of OH-oxidation of methacrolein obtained in this study at “free pH” (i.e. between 4.5 and 6.5) is in good agreement with those obtained by Buxton et al. (2000) at pH=4 and by Szeremeta et al. (2009) at pH=7 (see below Figure 1). Therefore, the pH value does not influence the kinetic rate constant of OH-oxidation of methacrolein under atmospheric conditions.

Specific comments 1: *One major concern for the study is the big change in pH of the studied solution, i.e. from 5.6 to 4.5. It would have been probably more interesting if the authors studied at least a few more pHs, e.g. pH = 3 and 2, since some of the aged cloud drops can reach pH of about 2.*

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The main goals of the study were to identify and quantify the reaction products, to establish a chemical mechanism of OH-oxidation of methacrolein, and to estimate the carbon yield. This study was done at “free pH” which is representative of the clean atmosphere. After the reaction, we observed a change of the pH value from 5.6 to 4.5 due to the formation of organic acids, thus indicating the aging of the solution. However, the suggestions of anonymous referee #1 to study the reaction at fixed pH values is of great interest, since it permits to study the impact of pH values on the branching ratios in the mechanism. Such experiments are our next objectives.

These comments will be added in the manuscript.

Specific comments 2: Also, the bimolecular rate constant the author reported is in good agreement with the one reported by Buxton et al. Since the value is already reported, the originality of the study is not granted.

Specific comments 3: Authors state that the slight difference in rate constant between the one they report and Buxton et al. is due to temperature change. If so, the authors also should have studied rate constant at 20 °C to confirm it. If the rate constants were reported at several temperatures, the results would have been much more interesting one.

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 :

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

Where:

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

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

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):

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

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):

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

Where:

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

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

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

At T = 298 K, we obtained:

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

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.

Number of saturated / unsaturated compounds	ΔG^\ddagger values (kJ.mol ⁻¹)			reference
	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.

Specific comments 4: Page 6407, line 24, about hydroperoxide. The authors state that it was not detected. There did not seem to appear any experimental techniques or detection limit for the peroxides analysis. They should be included in Table 1. Continued, which I suggest to change to Table 2 since the "Table 1" and "Table 1. Continued" have very different information.

As for most of the multifunctional organic compounds of this study, 3-hydroperoxy-2-hydroxy-2-methylpropanal (with a molecular weight of 120 g.mol⁻¹) was searched for using the ESI-MS. The signals obtained at 119 (at M-1 in the negative mode) and at 121 (at M+1 in the positive mode) corresponded to the background noise. This is the reason why we stated that this compound was not detected. However, its detection limit was not studied.

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This will be added in the corrected manuscript, together with the separation between "Table 1" and "Table 1 continued" which will be renamed to "Table 2"

Minor comments:

1 and 2 will be changed in the corrected manuscript.

3. Page 6401, 7th line, "4 mL samples were taken" It would be more useful to state that the volume of samples taken out corresponds to ? % change in volume relative to the initial volume. Otherwise, the statement itself does not mean much. Or, the initial volume of the sample should be stated.

4 mL is indeed the volume of each sample. The sentence "During the reaction, 4mL samples were taken at periodic intervals prior to chemical analysis" will be changed to "During the course of the reaction, at periodic intervals, aliquots of 4 mL were removed from the photoreactor prior to chemical analysis"

References

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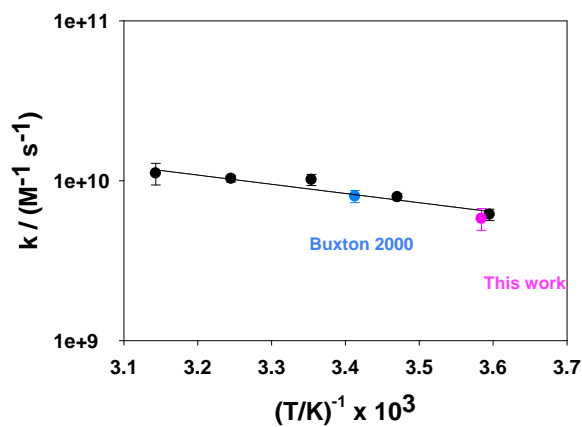


Figure.1 : Rate constants of OH-oxidation of methacrolein as a function of temperature: comparison between the values obtained by Szeremeta et al., (2009) at pH = 7 (black), Buxton et al. (2000) at pH = 4 (blue) and this work at « free pH » (pink).

Fig. 1.

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