

Interactive comment on “In-cloud processes of methacrolein under simulated conditions – Part 2: Formation of Secondary Organic Aerosol” by I. El Haddad et al.

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The authors thank referee #2 for his valuable comments that will be considered in the corrected manuscript. The authors answer, below, to the interrogations/comments of referee #2.

Comment 1: The experimental setup used here for the aqueous phase photo-oxidation of methacrolein is described in details in Liu et al., 2009 (companion paper entitled “*In-cloud processes of methacrolein under simulated conditions – Part 1: Aqueous phase photooxidation*”). The authors have used H_2O_2 associated to UV irradiation to generate OH radicals in the aqueous phase. The concentration of OH radicals was not

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measured but it can be estimated on the basis of kinetic calculations.

The mechanism of H₂O₂ photolysis is presented in Table 1.

Reaction	Rate constant at 298 K	Reference
$\text{H}_2\text{O}_2 + h\nu \longrightarrow 2 \cdot\text{OH}$	$J=1.8 \times 10^{-5} \text{s}^{-1}$	Poulain et al., 2007*
$\text{H}_2\text{O}_2 + \cdot\text{OH} \longrightarrow \text{HO}_2\cdot + \text{H}_2\text{O}$	$k_1=2.7 \times 10^7 \text{ M}^{-1}.\text{s}^{-1}$	Christensen et al., 1982
$\text{HO}_2\cdot \longleftrightarrow \text{H}^+ + \text{O}_2^{\cdot-}$	$\text{pKa}=4.8$	Bielski et al., 1978
$\text{HO}_2\cdot + \text{O}_2^{\cdot-} \longrightarrow \text{H}_2\text{O}_2 + \text{O}_2 + \text{HO}^-$	$k_2=8.2 \times 10^7 \text{ M}^{-1}.\text{s}^{-1}$	Christensen et al., 1988
$\cdot\text{OH} + \text{Macr} \longrightarrow \text{Products}$	$k_3=8.0 \times 10^9 \text{ M}^{-1}.\text{s}^{-1}$	Buxton et al., 2000

Table 1: mechanism of H₂O₂ photolysis and first step of OH-oxidation of methacrolein.

* measured using the same experimental protocol as in this work.

As indicated in the mechanism above, there is no O₃ production. Furthermore, O₃ can not be formed from OH-oxidation of methacrolein in the aqueous phase, as indicated by the mechanism developed in Liu et al., 2009 (companion paper : “*In-cloud processes of methacrolein under simulated conditions – Part 1: Aqueous phase photooxidation*”). Other radicals can be formed, such as HO₂[•] and O₂^{•-}. However, these oxidants are significantly less reactive than OH radicals, and their reactions towards molecular organic species are considered neither in photo-oxidation studies, nor in models (Monod and Carlier, 1999; Herrmann, 2003; Poulain et al., 2007; Ervens et al., 2003; Herrmann et al., 2005).

Assuming the quasi-stationary state for OH radicals,

$$\frac{d[\text{OH}]}{dt} = 2J[\text{H}_2\text{O}_2] - K_1[\text{OH}][\text{H}_2\text{O}_2] - K_3[\text{OH}][\text{Macr}]$$

$$\Rightarrow [\text{OH}]_t = \frac{2J}{K_1 + K_3} \frac{[\text{Macr}]_t}{[\text{H}_2\text{O}_2]_t}$$

One obtains, at the initial reaction time (t=0):

$$[\text{OH}]_0 = \frac{2J}{K_1 + K_3} \frac{[\text{Macr}]_0}{[\text{H}_2\text{O}_2]_0} = 2.8 \times 10^{-13} \text{ M}$$

The obtained OH concentration is of the same order as the concentrations ($3 \times 10^{-13} \text{ M}$)

predicted by cloud chemistry models (Monod and Carlier, 1999; Ervens et al., 2003; Deguillaume et al., 2004; Herrmann et al., 2005).

Comment 2: Referee #2 has pointed out the possible reaction between Methacrolein and H_2O_2 . Even though several previous studies have considered the direct reaction of methacrolein with H_2O_2 , it was verified, in this work (see: Liu et al., 2009), that under our experimental conditions, this reaction can be neglected compared to OH-oxidation: No significant decrease of the methacrolein concentrations was observed, even after 24 hours, in the presence of H_2O_2 , in the dark. These complementary information are described in the companion paper (Liu et al., 2009), thus no complementary precision will be added in the manuscript.

Comment 3: Our preliminary tests (described in the companion paper by Liu et al., 2009) have shown that no significant decrease of the concentrations of methacrolein was observed, even after 24 hours,

1. in the presence of H_2O_2 , in the dark,
2. in the absence of H_2O_2 , under UV-visible irradiation

These kinds of tests have also been carried out in the past on other organic molecules, such as methanol, acetone, N-methylpyrrolidone, ... This shows that, at least in the absence of OH radicals, the heterogeneous reactions on the walls are of negligible importance. Moreover, in the aqueous phase, the diffusion time is much slower than in the gas phase (by a factor of 250, due to typical diffusion coefficients), therefore, the wall effects are usually not considered, especially for radicals such as OH whose life time is of the order of 1 second.

Comment 4: The authors are aware that the yields obtained depend on several experimental parameters such as the reactant (methacrolein and OH radical) concentrations, composition of the aqueous matrix (salt, organics..) In addition, in our case

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the yield depends also on the setup used to produce SOA (nebulisation/evaporation). Although particle transmission efficiencies can slightly differ between organic and inorganic particles, NaCl have been chosen to estimate the transmission efficiency of particles from our experimental setup for 2 reasons: First NaCl is exclusively in the particulate phase which is not the case for most of the organic species and secondly because both Na^+ and Cl^- can be analysed with a high level of confidence in both aqueous and particulate phases. In addition, the yield estimation calculated by this approach is in good agreement with the one determined using an independent calculation method (that does not assimilate the transmission efficiencies of the aerosol in the system) developed in Michaud et al., 2009 (companion paper entitled “*In-cloud processes of methacrolein under simulated conditions – Part 3: Hygroscopic and volatility properties of the formed Secondary Organic Aerosol*”). This result provides some confidence on these estimations. In the corrected manuscript, cautions that have to be taken when using these yields will be mentioned more clearly.

Comment 5: Other radicals present in the tropospheric aqueous phase can react towards soluble organic compounds such as NO_3^\bullet , Cl^\bullet , $\text{SO}_4^{\bullet-}$ However, the modelling studies of Ervens et al., 2004 show that the OH radicals are the major oxidant in the tropospheric aqueous phase. Precisions regarding the implication of other radicals will be added in the conclusion section.

References:

Bielski, B.H.J.: Reevaluation of the spectral and kinetic properties of HO_2 and O_2 free radicals, Photochem. and Photobiol., 28, 645-649, 1978.

Buxton, G.V., Salmon, G.A. and Williams, J.E.: The reactivity of biogenic monoterpenes towards OH and SO_4^- radicals in De-oxygenated acidic solution, J. Atmos. Chem. 36, 111-134, 2000.

Christensen, H., Sehested K. and Corfitzen H.: Reactions of hydroxyl radicals with hydrogen peroxide at ambient and elevated temperatures, J. Phys. Chem., 86, 1588-1590, 1982

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Christensen H. and Sehested K.: HO₂ and O₂⁻ radicals at elevated temperatures, J. Phys. Chem., 92, 3007-3011, 1988.

Deguillaume, L., Leriche, M., Monod, A., and Chaumerliac, N.: The role of transition metal ions on HOx radicals in clouds: a numerical evaluation of its impact on multiphase chemistry, Atmos. Chem. Phys., 4, 1–16, 2004.

Ervens, B., George, C., Williams, J. E., Buxton, G.V., Salmon, G.A., Bydder, M., Wilkinson, F., Dentener, F., Mirabel, P., Wolke, R., and Herrmann, H.: CAPRAM 2.4 (MODAC mechanism): An extended and condensed tropospheric aqueous phase mechanism and its application. J. Geophys. Res., 108, D14, 4426, 2003.

Herrmann, H., Tilgner, A., Barzaghi, P., Majdik, Z., Gligorovski, S., Poulain, L. and Monod, A.: Towards a more detailed description of tropospheric aqueous phase organic chemistry: CAPRAM 3.0. Atmos. Environ. 39, 4351–4363, 2005.

Liu, Y., El Haddad, I., Scarfogliero, M., Nieto-Gligorovski, L., Temime-Roussel, B., Quivet, E., Marchand, N., Picquet-Varrault, B. and Monod, A.: In-cloud processes of methacrolein under simulated conditions – Part 1: Aqueous phase photooxidation, Atmos. Chem. Phys. Discuss., 9, 6397-6424, 2009.

Michaud, V., El Haddad, I., Liu, Y., Sellegri, K., Laj, P., Villani, P., Picard, D., Marchand, N., and Monod, A.: In-cloud processes of methacrolein under simulated conditions – Part 3: Hygroscopic and volatility properties of the formed Secondary Organic Aerosol, Atmos. Chem. Phys. Discuss., 9, 6451-6482, 2009.

Monod, A. and Patrick Carlier: Impact of clouds on the tropospheric ozone budget: Direct effect of multiphase photochemistry of soluble organic compounds. Atmos. Environ. 33, 4431-4446, 1999.

Poulain, L., Monod, A. and Wortham, H.: Development of a new on-line mass spectrometer to study the reactivity of soluble organic compounds in the aqueous phase under tropospheric conditions: Application to OH-oxidation of N-methylpyrrolidone. J. Photochem. Photobio. A-Chem., 187, 10-23, 2007.

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 6425, 2009.

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