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Interactive comment on "The kinetics and mechanism of an aqueous phase isoprene reaction with hydroxy radical" *by* D. Huang et al.

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To Dr. Brigante

Thanks for your effort and constructive comments. Here are our responses to your comments:

(Q1) Adopted aqueous solution is not representative of real cloud water composition and abstract should be changed (see page 8516 lines 4 and 5). The authors analyzed aqueous oxidation of isoprene toward OH radical and not in cloud water. Considering the chemical composition of used solutions and the missed experimental OH radical formation rate determination this study seems to be far from really understand the fate of isoprene in clouds.

(A1) We have revised the "we analyzed the aqueous oxidation of isoprene in clouds and its reaction products" into "we analyzed the aqueous OH-initiated oxidation of isoprene and its reaction products regarding the acidity and temperature as in-cloudy conditions" (page 8516 lines 4 and 5). As you point out, the adopted aqueous solution is indeed far from the real clouds which contains various inorganic and organic compounds and has a specific OH radical formation rate. Currently it is very difficult to take all the variables into account to investigate the aqueous isoprene fate. However, the basic constituent of cloud is water. We think that understanding the isoprene reaction relative to pure water is a preliminary work to understand its fate in the real cloud. A number of groups have studied the chemical processes in cloud via understanding the chemical processes in water at certain pH and temperature (Seinfeld and Pandis, 2006; Altieri et al., 2008; El Haddad et al., 2009; Liu et al., 2009; Michaud et al., 2009). After knowing the water effect on the isoprene transformation at first, which is the topic of the present work, one can further study the complicated fate of isoprene by adding inorganic ions and/or organics into water. We highly appreciate your suggestion about the concentration determination of OH radicals. We have performed an experiment for determining the OH concentration profile using salicylic acid.

Reference: Seinfeld, J. H. and Pandis, S. N.: Atmospheric Chemistry and Physics, second edition, John Wiley Sons, 2006. Altieri, K. E., Seitzingera, S. P., Carlton, A. G., Turpin, B. J., Klein, G. C., and Marshall, A. G.: Oligomers formed through in-cloud methylglyoxal reactions: chemical composition, properties, and mechanisms investigated by ultra-high resolution FT-ICR mass spectrometry, Atmos. Environ., 42, 1476–1490, 2008. El Haddad, I. E., Liu, Y., Nieto-Gligorovski, L., Michaud, V., Temime-Roussel, B., Quivet, E., Marchand, N., Sellegri, K., and Monod, A.: In-cloud processes of methacrolein under simulated conditions – Part 2: formation of secondary organic aerosol, Atmos. Chem. Phys., 9, 5107–5117, doi:10.5194/acp-9-5107-2009, 2009. 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., 9, 5093–5105, 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., 9, 5119–5130, 2009.

(Q2) Lamp emission wavelengths are missed in the Experimental section (2.2 apparatus and procedure). Using a Xenon arc lamp and a quartz reactor wavelength < 240 nm are not stopped and are certainly responsible for the isoprene direct degradation.

(A2) We have provided the lamp wavelength in the experimental section, that is, 250-380 nm. In the control experiments, the concentration of isoprene as well as MAC/MVK/mixed standard solution fluctuates within the tolerance range (<6 percent of initial concentration) during the 6 h irradiation. We have discussed more about the control experiments in our revised manuscript.

(Q3) In order to better understand the "real" fate of isoprene in clouds a comparison with the OH radical formation rates (M s^{-1}) is needed.

(A3) Yes, the comparison is imporant. We use SA as a scavenger during the photolysis of H2O2 solution, and presume that all the OH radical react with SA, because the k_{SA-OH} (2.2*10^{10} M^{-1} s^{-1}) is much higher than the rate constant of H_2O_2 react with OH ($k_{H2O2-OH}$ = 2.7*10^{7} M^{-1} s^{-1}) which is a main competitive pathway for the OH loss in the aqueous solution. Thus, the OH formation rate translates into the rate of the formation rate of the OH addition product of SA. The formation rate of 2,5-dihydroxybenzic acid which is a main OH addition product of SA is determined to be 2.0*10^{-9} M s^{-1} in the first 20 min irradiation. This value is the lower limit, because the OH addition product of SA could also react with OH radical and another main OH addition product of SA 2,3-dihydroxybenzic acid was not quantify limited to the present technique. However, we have not enough materials about the OH formation rate in the real clouds.

(Q4) Why the averaged concentration of OH radical was estimated on the basis of

model simulation and not directly determined using an appropriate scavenger (section 3.2.1)? Certainly as demonstrated for isoprene degradation, model simulation lacks some reaction and probably a comparison with experimental OH radical quantification should be more appreciated.

(A4) Yes, there are many uncertainties for the modeled concentration of OH radical. We have re-estimated the rate constant of aqueous phase OH-oxidation of isoprene using salicylic acid as a reference compound.

(Q5) How the authors explain the fact that after 45 min a plateau is reached in figure 5? Hydrogen peroxide is still present in aqueous solution?

(A5) We monitored the concentration-time profile of H_2O_2 during the 6 h experiment process, and the H_2O_2 concentration was observed to be consumed by 4 percent after 45 min irradiation. A possible explanation is given in section 3.2.2, Explaining the mechanism of MG and GL formation, page 8535, line 15 to 24, that is, the decomposition of high molecular weight compounds. Nevertheless, there is not enough evidence for this explanation, further study is needed.

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 8515, 2011.