Atmos. Chem. Phys. Discuss., 11, C4293–C4299, 2011
www.atmos-chem-phys-discuss.net/11/C4293/2011/

Atmospheric
Chemistry
and Physics
Discussions

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

D. Huang et al.

zmchen@pku.edu.cn

Received and published: 4 June 2011

To Reviewer 1

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

(Q1) It is very unlikely that substantial amounts of isoprene will undergo phase transfer due to its very hydrophobic nature even if a reactive sink will be active such as a fast OH(aq)- isoprene reaction. I think that much more carbon will be transferred from the gas phase into the atmospheric aqueous phase because of uptake of the degradation products such as MVK and MACR. The study is interesting because of the kinetics results and the split of identified products but maybe it would better be published in a more specialized journal where kinetic and mechanistic questions can be discussed.

(A1) We accept that isoprene transfer into the aqueous bulk may not important for its overall aqueous chemistry. We have discussed the relative importance of the aqueous isoprene oxidation regarding the interface processes and why we present our work in the Atmospheric Chemistry and Physics. The details can be found in the former reply.

Like isoprene, MVK and MACR would react with oxidants in the bulk as well as on the surface of the droplets, although the ratio of these two pathways is unknown. As you point out, more MVK/MACR than isoprene will participate in the bulk reaction because of their higher solubility. Once isoprene contacts the surface of droplets, it will immediately react with the oxidants on the surface following a aqueous phase mechanism. Here we try to study this mechanism. As for MVK and MACR, we have reported their aqueous phase oxidation mechanisms by ozone and OH radical in our previous works (Chen et al., ACP, 2008; Zhang et al., ACP, 2010). The present study will further complete the fate of isoprene and its oxidation products and effect on the chemical composition of cloud/fog/wet aerosol in the atmosphere. We would like to present a series of studies for atmospheric aqueous oxidation of isoprene and MVK/MACR in ACP.

Reference: Chen Z.M., Wang H.L., Zhu L.H., Wang C.X., Jie C.Y. and Hua W.: A potentially important source of atmospheric aqueous oxidants: Aqueous phase ozonolysis of methacrolein and methyl vinyl ketone. Atmos. Chem. Phys., 8, 2255–2265, 2008. Zhang, X., Chen, Z. M., and Zhao, Y.: Laboratory simulation for the aqueous OH-oxidation of methyl vinyl ketone and methacrolein: Significance to the in-cloud SOA production, Atmos. Chem. Phys., 10, 9551–9561, doi: 10.5194/acp-10-9551-2010, 2010.

(Q2) Apparently, the carbon-balance based on the classical isoprene products is far from closed but other products significantly contributing were not identified. There are many unclear passages. The language of the manuscript needs to be checked. As a bottomline, the manuscript should be re-written. A possible significance of this work must be identified and justified.

(A2) Yes, the carbon balance is observed as 50 percent of total carbon because of the limitation of our current techniques. We have mentioned in the manuscript that the missing carbon are possibly CO/CO_2, high molecular weight compounds (HMWs), etc. Currently, it is difficult to determine the HMWs especially for quantifying them (e.g., Liu et al, 2009; Schwier et al., 2010). In the present work, we tell the readers the difference between the gas and aqueous phase oxidation of isoprene by quantifying the "classical isoprene products". Obviously, a further study is needed to know these missing products although this is a great challenge.

We have tried our best to revise the language and unclear passages in the revised version.

Reference: 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. Schwier, A. N., Sareen, N., Mitroo, D., Shapiro, E. L., and McNeill, V. F.: Glyoxal-methylglyoxal cross-reactions in secondary organic aerosol formation, Environ. Sci. Technol., 44, 6174–6182, 2010.

(Q3) Details Page 8518, line 1: The solubilities of MVK and MACR are much higher than the one of isoprene, so where is the atmospheric relevance? Refenceing to these investigations is not useful.

(A3) We agree with you that the solubility of MVK and MACR are much higher than that of isoprene. Here we try to describe a history about the aqueous oxidation investigations from the highly-soluble oxygenated volatile organic compounds (OVOCs) (alcohols and aldehydes) to the moderately-soluble OVOCs (MACR and MVK), and then to the poorly-soluble VOCs (terpenes). Seinfeld and Pandis have pointed out in their book that "The above analysis suggests that species with a Henry's law coefficient

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

lower than about 1000 M atm^{-1} will partition strongly toward the gas phase and are considered relatively insoluble for atmospheric applications. Species with Henry's law coefficients between 1000 and 10000 M atm $^{-1}$ are moderately soluble, and species will even higher Henry's law coefficients are considered very soluble. As can be seen from Table 7.2, remarkably few gases fall into the very soluble category. This does not imply, however, that only very soluble gases are important in atmospheric aqueous-phase chemistry." (Seinfeld and Pandis, 2006). For example, SO_2 has a Henry's law coefficient of 1.23 M atm^{-1} at 298 K, however, its aqueous oxidation is considered to be an important pathway for its transformation in the atmosphere. Recently, the aqueous phase oxidation of VOCs is considered to be a potential contributor to the SOA formation (e.g., Yu et al., 2008; Enami et al., 2010).

Reference: Seinfeld, J. H. and Pandis, S. N.: From Air Pollution to Climate Change, Atmospheric Chemistry and Physics, second edition, Wiley, New York, page 290, 2006. Yu, Y., Ezell, M. J., Zelenyuk, A., Imre, D., Alexander, L., Ortega, J., Thomas, J. L., Gogna, K., Tobias, D. J., D'Anna, B., Harmon, C. W., Johnson, S. N., and Finlayson-Pitts, B. J.: Nitrate ion photochemistry at interfaces: a new mechanism for oxidation of a-pinene, Phys. Chem. Chem. Phys., 10, 3063–3071, 2008. Enami, S., Hoffmann, M. R., and Colussi, A. J.: Prompt formation of organic acids in pulse ozonation of terpenes on aqueous surfaces, J. Phys. Chem. Lett., 1, 2374–2379, 2010.

(Q4) Page 8518, line 22: 'Due to the...' – Sentences like this are not needed in a scientific contribution. It is known that liquid water is different from gas phase water. The rest of the paragraph is not necessary.

(A4). Yes, we have deleted this paragraph in our revised manuscript.

(Q5) Page 8522, line 22: It is good to see that the authors tried to build a box model for isoprene aqueous phase chemistry but, again, is that needed really? When the model is coupled to the gas phase, which fraction of isoprene is being transferred to aqueous particles? Demonstrate a potential significance of this work!

(A5). The box model can help us better understand the mechanism of aqueous isoprene-OH reaction and the water effect on the yields and distributions of isoprene products comparing with the corresponding gas phase reaction. When the model is coupled to the gas phase, the reactive uptake of isoprene from the gas phase is the key process, and this process may be controlled not only by its Henry's law constant. Unfortunately, currently we cannot give an exact fraction. Noticeably, the interface reaction has not been considered into the current models. The significance of this work has been discussed in the former reply.

(Q6) Apparently, in the construction of the mechanism, many estimates have been used. Are these all valid? The comparison of measure against model concentration-time profiles are surprisingly good (Fig. 4, 6 and 8).

(A6) In the mechanism, there are three major assumptions: (1) the branching ratios of the six hydroxy isoprene peroxyl radical produced by OH radical addition to isoprene are the same as the gas phase reaction; (2) the rate constants (in units of M^{-1} s^{-1}) of aqueous phase oxygenated radical reactions are estimated to be four orders of magnitude lower than those (in units of cm^3 mol^{-1} s^{-1}) in the corresponding gas phase reactions; (3) in the aqueous phase, the rate constant of the self-reaction between $R2O_2$ radicals may increase and is at the same level with the other five $R_{hip}O_2$ radicals, because that the $R2O_2$ radical is the most hydrophobic, causing the aggregation of $R2O_2$ radical in water, whereas $R2O_2$ radical is considered to be not as active as the other five $R_{hip}O_2$ radicals in the gas phase . At present, we cannot exactly validate the applicability of these assumptions in the aqueous phase chemical processes. However, what we do is based on the previous laboratory and theoretical studies, as shown in section 2.6 (for the assumptions (1) and (2)) and section 3.2.2 page 8531, line 5 to page 8532, line 15 (for the assumption (3)) of the manuscript.

Figure 4 is not a model-measurement comparison result but a variation in abundance of the ionic molecules detected by high-performance liquid chromatography-electrospray ionization-mass spectrometry during the aqueous oxidation of isoprene.

Figure 6 is the model-measurement comparison result for isoprene, MACR, and MVK. It is logical for isoprene to have a good comparison between the measure and the model concentration-time profiles, because in the model we applied a rate constant of the aqueous isoprene-OH reaction which was determined by monitoring the aqueous concentration of isoprene. As shown in section 3.2.2 page 8530, line 20 to 24, and page 8532, line 10 to 16, the comparison of measure against model concentration-time profiles for MACR and MVK is bad when the model simulation is performed with the initial kinetic parameters (Fig. 6a), and is good when the model simulation is performed with the adjusted kinetic parameters (Fig. 6b). This good comparison is because of our enhancing the rate constant of the self-reaction between $R2O_2$ radicals based on the assumption (3) mentioned above. To further validate the hypothesis that the $R2O_2$ self-reaction would be enhanced by water, we carried out a sensitivity analysis by adjusting the rate constants of self- and cross-reactions (ks and kc) for the six $R_{hip}O_2$ radicals as shown in Fig. 7(section 3.2.2 explaining the ratio of MVK to MACR, page 8532, line 16 to page 8533, line 8). The sensitivity analysis result supports our hypothesis.

As Fig. 8 shows, the modeled production of MG and GL by pathway of aqueous MAC/MVK-OH reaction cannot match with that measured in the aqueous isoprene-OH reaction. Accordingly, we add two more pathways in the aqueous mechanism for producing MG and GL, referring to two other gas phase models, i.e., the Mainz Isoprene Mechanism 2 (MIM2) (Taraborrelli et al., 2009) and the isoprene photooxidation mechanism described in the Regional Acid Deposition Model 2 (RADM2) (Zimmermann and Poppe, 1996). We find that the modified model can well predict the MG and GL concentrations in the first stage of the reaction (MG and GL increase gradually), but fail to predict the second stage (an MG plateau) and the third stage (MG and GL declines; Fig. 11).

(Q7) What are the main sensitivities of the modeled curves in the aqueous phase mechanism?

(A7) As we have mentioned in the section 3.2.2, Explaining the ratio of MVK to MACR,

Full Screen / Esc
Printer-friendly Version
Interactive Discussion
Discussion Paper

the rate constant for the $R2O_2$ self reaction is enhanced to the same order of magnitude as the rate constants for the other $R_{hip}O_2$ self-reactions in the aqueous model, whereas the value for the $R2O_2$ radical is two orders of magnitude lower than those of the other five radicals in the gas phase. To further validate the hypothesis that the $R2O_2$ self-reaction would be enhanced by water, we carried out a sensitivity analysis by adjusting the rate constants of self- and cross-reactions (ks and kc) for the six $R_{hip}O_2$ radicals. The model responses, represented by MVK and MACR concentrations as a function of time, are as follows: (i) When all the ks and kc values were simultaneously raised or lowered by two orders of magnitude, the predicted concentrations for MVK and MACR were almost the same as those predicted by the corresponding initial or $R2O_2$-adjusted model (Fig. 7a and Fig. 7b). Thus, simultaneously changing the rate constants for the self- and cross-reactions of the six $R_{hip}O_2$ radicals could not change the product branching distributions. (ii) When the ks and kc for the $R6O_2$ radical in the initial model were lowered by two orders of magnitude (because the high ratio of MVK/MACR may also be caused by the inhibition of MACR production), the maximum MVK concentration increased by 14.8

In addition, We have added a kinetic experiment. A competition kinetics method was employed to determine the rate constants of OH oxidation of isoprene, MACR, and MVK, using salicylic acid as a reference compound. Accordingly, we have replaced the Figure. S2 in the supplementary material by the competition kinetics curves. We have used the newly determined three rate constants in the box model, and renewed the corresponding modeled data and figures. We have added the aqueous OH oxidation mechanism of MACR and MVK into Table. S1 in the supplementary material according to the reviewer's suggestion.

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