

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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Received and published: 27 April 2011

To Reviewer 1 and Reviewer 2

Thanks for your effort and constructive comments. We think that you may most concern about two questions, namely, (1) the relative importance of the aqueous isoprene oxidation in the atmosphere and (2) the significance of our present work on the aqueous bulk oxidation of isoprene. Here are our responses to these two questions, and other technical comments will be answered in another reply.

(1) The relative importance of the aqueous isoprene oxidation in the atmosphere

We agree that the aqueous bulk oxidation of isoprene may be not important compared with its gas phase chemistry, because the solubility of isoprene is limited by its

C2291

small Henry's Law constant. However, we think that the surface reaction occurring on droplets might be important for the oxidation of isoprene with OH radicals. The aqueous phase reaction includes not only the reaction in the bulk of droplets but also the reaction on the surface of droplets. Moreover, nanometer-size water clusters, $(\text{H}_2\text{O})_n$, which are ubiquitous in the atmosphere, are considered to potentially participate in the atmospheric chemistry (Ryzhkov et al., 2006; Sennikov et al., 2005). Therefore, generalized aqueous phase oxidation of organic compounds in the atmosphere can be categorized into three chemical scenarios (Fig.6 in Chen et al., 2008): (i) in scenario 1 (the bulk reaction), both oxidant and organic compound stay and react in the aqueous phase; (ii) in scenario 2a and scenario 2b (the interfacial reaction), one reactant stays in the aqueous phase and reacts, via collision, with another reactant from the gas phase; and (iii) in scenario 3 (the interfacial reaction), neither oxidant nor organic compound stays in the aqueous phase but both can contact the aqueous phase simultaneously from the gas phase and react at the instant of contact. These scenarios may enlarge the aqueous phase reaction scope than that considered usually in previous multiphase chemical models. Then, what is the percentage for each of the three reaction scenarios? This needs further laboratory and modeling studies. However, we strongly recommend the reaction on the surface of droplets including scenario 2 and scenario 3 is significant for a rapid reaction such as the OH-initiated oxidation of isoprene. Furthermore, Pöschl et al. (2007) suggested a double-layer surface model, “which comprises two monomolecular layers: a quasi-static surface layer consisting of (quasi-)non-volatile particle components Y_j (molecules, ions, or functional groups), and a sorption layer consisting of adsorbed volatile molecules X_i (Fig. 2). Both the non-volatile particle components Y_j and the volatile molecules X_i can be reversibly transferred between the double-layer surface and the underlying particle bulk, in which they can undergo diffusion and reaction”. If so, the Henry's Law constant mentioned previously would no longer be a key factor restricting the aqueous phase reaction. In fact, Finlayson-Pitts and Pitts described in their book (Finlayson-Pitts and Pitts, 2000) that “Henry's Law can be applied to predict solution concentrations only if certain conditions

C2292

are met. Thus it assumes that there are no irreversible chemical reactions that are so fast that the equilibrium cannot be established. It also assumes that the surface of the droplet is an unimpeded air-water interface". In this way, when isoprene molecule is impeded on the surface of aqueous droplet, there may be another concentration scenario that is different from that predicted by Henry's Law.

To our knowledge, in recent years there have been many studies focused on the aqueous surface/interface adsorption or oxidation of volatile organic compounds (VOC). Goss (2004) emphasized that adsorption (on the surface) is different from absorption (into the bulk), and the summation of these two parts represents the aqueous VOC and SVOC quantity after their partitioning between the gas phase and condensed phases. Some research groups studied the aqueous surface/interface adsorption of poorly-soluble gases and generally found a much higher interface concentration compared to the gas phase concentration. For example, Vácha et al. (2004) calculated the free energy profiles associated with moving atmospheric gases or radicals (N_2 , O_2 , O_3 , OH, H_2O , HO_2 , and H_2O_2) across the air/water interface, and then they estimated the concentrations of these species in the gas phase, aqueous interface, and aqueous bulk. Their result showed that the average aqueous interface concentration (C_{aqi}) was much higher than the corresponding gas phase concentration (C_g) and aqueous bulk concentration (C_{aqb}). For example, the ratios of C_{aqi}/C_g are 3.62 for O_3 , 8800 for OH radical, and 2.6×10^7 for H_2O_2 , the ratios of C_{aqi}/C_{aqb} are 11 for O_3 , 8 for OH radical, and 1.5 for H_2O_2 . Interestingly, the ratio of C_{aqi}/C_{aqb} (11) for the poorly-soluble O_3 is much higher than that (1.5) of the soluble H_2O_2 . It is likely that the aqueous interface concentration of hydrophobic gas would be much higher than the calculated concentrations based on the Henry's Law constant. So, we expect that isoprene would undergo a similar fate as O_3 does, namely, the interface concentration of isoprene may be much higher than its gas phase and aqueous bulk concentrations. If combining the interface concentrations of OH and isoprene, it is expected that the interface reaction of isoprene with OH would be of much more important than the reaction in the aqueous bulk phase based on the assumption that the interface rate constant for the reaction of isoprene

C2293

and OH is comparative or even higher than that in the gas phase. Before this, as it should be, the atmospheric applicability of the calculated result of Vácha et al. (2004) needs further investigation. In addition, Reid and Sayer (2002) pointed out that "Solute molecules may preferentially adsorb to the interface rather than undergoing full solvation in the bulk liquid phase. Full solvation may lead to such disruption of the hydrogenbonding network of water molecules that the energetically most favourable position for the solute is adsorption at the interface". Other works have also provided a similar view about the enhancement of interface concentration (Donaldson and Anderson, 1999; Ghosal et al., 2005). It can be concluded that the surface/interface concentration of a compound is higher than the homogeneous phase concentration. Moreover, in a fast aqueous reaction system, the amount of a reactant participating in the reaction is determined not only by its thermal dynamic equilibrium concentration but also by its reaction kinetic rate. If the kinetic rate is fast enough, the thermal dynamic gas-liquid equilibrium would not be achieved, resulting in a much larger amount of this reactant into the aqueous phase from the gas phase.

In addition, experimental evidence indicates a reactive uptake of VOC by atmospheric water droplet, such as the interface reaction could facilitate the mass transfer, and the enhanced concentration of a reactant at the interface may increase the probability of encounter of another reactant with adsorbed molecules (Raja and Valsaraj, 2006). Mmereki et al. (2004) experimentally investigated the interface reaction of gas phase ozone with anthracene adsorbed at the aqueous interface, and suggested that the interface ozone oxidation of anthracene may be of comparable importance to the gas phase oxidation by OH. Similar works can be seen in the literatures (Mmereki and Donaldson, 2003; Kahan and Donaldson, 2007). One can say that the polycyclic aromatic hydrocarbon (PAH) and other previous research objects are not as volatile as the object isoprene investigated in our present work, and it may be easier for PAH to adsorb on droplets and react on the surface. However, the rate constant of the gas OH-initiated oxidation ($1.0 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) of isoprene are higher than or comparable with that of PAH (2.3×10^{-11} for naphthalene, 5.8×10^{-11} for acenaphthene, 1.3×10^{-11}

C2294

for fluorene, 2.7×10^{-11} for phenanthrene, 1.1×10^{-11} for fluoranthene, and 1.9×10^{-10} for anthracene in units of $\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ measured by Brubaker and Hites, 1998), and the fact that atmospheric isoprene concentration (0.1–7 ppbv) (Kuhlmann et al., 2004) is several orders of magnitude higher than that of PAH (several pptv) (Mandalakis et al., 2002) needs to be considered. In a recent related work, Enami et al. (2010) reported the fast reaction of terpene with ozone on aqueous surfaces and observed carboxylic acids in <10 us once the gas phase ozone collisions with the surface of aqueous terpene solutions happened, indicating a potential SOA contribution pathway for the aqueous oxidation of poorly-soluble organic compounds. Moreover, Yu et al. (2008) reported that the average residence time of alpha-pinene adsorbing onto the aqueous interface was more than 0.1 ns in their study of nitrate ion photochemistry oxidation of alpha-pinene at the aqueous interface, and within 1 ns alpha-pinene resided near the interface, thus the time was enough for the reaction of alpha-pinene and the OH radical produced by the nitrate photolysis. For the aqueous isoprene–OH reaction, the hydrophilia of isoprene is similar to alpha-pinene, and the reactivity of isoprene is higher than alpha-pinene, so it is possibly important for isoprene to react with OH radical at the interface of various aqueous solutions in the real atmosphere. In summary, all the studies mentioned above indicate that the relative importance of aqueous reaction of a compound is not determined completely by its Henry's Law constant. In an overview, Kolb et al., (2010) indicated that the surface activity, concentration, and impact of adsorbed compounds by aqueous particles need further studies. Consequently, we suggest that the aqueous oxidation might be a potential sink of isoprene in cloud/fog/wet aerosol, or inversely, the aqueous isoprene oxidation would modify (age) the aerosols, although currently we have not quantified this sink or modification yet. Obviously, the cloud/fog/wet aerosol environment provides a huge amount of water molecules in forms of droplet, cluster and adsorbate, and these water molecules will significantly affect the product yield and distribution of VOC oxidation.

(2) The significance of our present work on the aqueous bulk oxidation of isoprene

C2295

For isoprene, it would be better to study its surface oxidation on droplets. However, there is a big challenge for investigating this surface reaction. This challenge arises from the interference of the gas phase reaction. It is a difficult task for us to exclude the gas phase reaction during performing the surface reaction of isoprene because of its high volatility and reactivity and to prevent the gas phase products entering into the aqueous phase, resulting in large uncertainties in determination of the product yield and distribution. In addition, there are great uncertainties for the evaluation of the surface area of droplets, and it is now difficult for us to simultaneously get the size distribution of droplets and to collect the droplets for quantitative analysis. These problems may significantly affect the estimation of the condensed water effect on the oxidation of isoprene. Therefore, in the first place, we intended to investigate the aqueous bulk oxidation of isoprene to identify the condensed water effect on the product distribution and yield of the isoprene oxidation, and to quantitatively tell the difference between the gas phase and aqueous phase reactions. Next, we would like to study the aqueous surface reaction of isoprene when our equipment and the monitoring technique are available. In the future, we can make a comparison between the bulk and surface reactions.

We think the chemical pathways proposed in this study are possibly applicable to the surface reaction of the droplets. Although the bulk OH-oxidation rate constant may be significantly different from that on the aqueous surface, our work provide a value which can be used for reference for the corresponding aqueous surface study. We expect that our present study could add to the increasing body of literatures that cloud/fog/wet aerosol processing contributes to the SOA formation in the atmosphere. In addition, our present study is also related to the ocean isoprene SOA in the sea salt aerosol. Increasing evidence has indicated that the ocean emission is a source of isoprene in the ocean boundary layer (Milne et al., 1995; Shaw et al., 2003; Broadgate et al., 2004; Sinha et al., 2007), and field measurement has revealed the SOA existing in the sea aerosol (Cai and Griffin, 2003; Gantt et al., 2010; Miyazaki et al., 2010). The isoprene produced by the phytoplankton could react with OH radical in the sea water before entering into the atmosphere across the water-air interface, and this process

C2296

would contribute to the sea salt aerosol components. It is well known that the sea salt aerosol arises from the spray of the sea surface water and its evaporation. One hand, this sea salt aerosol possibly contains isoprene SOA components produced in the sea water interface and bulk OH-initiated oxidation of isoprene. Another hand, this aqueous phase reaction would result in an underestimation of isoprene emission by ocean.

We think that the present study is a sequel of our previous works about the aqueous phase oxidation of isoprene and its oxidation products published in the *Atmospheric Chemistry and Physics (ACP)* (Chen et al., 2008; Zhang et al., 2010), and is also a commencement of the study on the aqueous surface reaction for isoprene. We are trying to explore a possible important oxidation pathway for the large biogenic organic compounds. Thus, we think *ACP* is a proper journal for publishing the series of our works.

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C2297

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C2298

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C2299

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

C2300