

Interactive comment on “Influence of Relative Humidity on the Heterogeneous Oxidation of Secondary Organic Aerosol” by Ziyue Li et al.

Anonymous Referee #2

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This study investigated the influence of RH on heterogeneous OH oxidation of a-pinene SOA using laboratory experiments combined with kinetic modeling. They found that SOA evaporated much stronger when oxidized under high RH, which is attributed to RH-dependent differences in the OH uptake coefficient and/or the net probability of fragmentation. The experiments were conducted using an aerosol flow tube and chemical composition was detected using VUV-AMS. I found that experiments were very sophisticated and conducted very well. Application of a kinetic model appears to provide useful insights, but the model does not treat gas diffusion of OH radicals, which appears to be a major limitation of this modeling approach. The manuscript is written overall well and I support publication of this manuscript if the following comments can be addressed and implemented in the revised manuscript.

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1. With high uptake coefficients (as OH uptake in this study), it is very important and critical to properly account for gas-phase diffusion for accurate interpretation and analysis of OH uptake (especially if $\Gamma > 0.1$). High uptake of OH would lead to depletion of OH in the near-surface gas phase, leading to build up of strong concentration gradients in the gas phase (see textbook such as Seinfeld and Pandis, 2006 etc.). In eq(3), [OH] was used to calculate a collision flux, and I suppose that the author meant average gas-phase OH concentrations with [OH]: this equation would need to be corrected (as OH concentrations close to particles would be depleted) to account for effects of gas-phase diffusion [see, for example, Poschl et al., ACP, 7, 5989, 2010]. Given that the model does not treat gas-phase diffusion, I am not convinced by quantitative conclusions of uptake coefficients (such as $0.2 > \Gamma > 0.1$, etc.). The lack of gas-phase diffusion treatment appears to be a major weakness of this study (it is not hard to implement this effect, so I encourage authors to implement). If the authors have any evidence that the effects of gas diffusion would be negligible in this study, this should be presented clearly. Without gas diffusion corrections, uptake coefficient you use is not a true uptake coefficient but should be termed as an effective uptake coefficient.

2. Recent studies have shown that ROOH would decompose to form OH and organic radicals under dark [Tong et al., ACP, 16, 1761, 2016] and light conditions [Badali et al., 15, 7831, 2015]. Peroxides contained in a-pinene SOA are shown to be labile [e.g., Epstein et al., EST, 19, 11251, 2014; Krapf et al., Chem, 1, 603, 2016]. In this study, ROOH were treated as stable compounds. I wonder if decomposition of ROOH would have implications on interpretation/analysis of your experiments.

3. Discussion in P23 is very interesting. Slade et al. (GRL, 44, 1583, 2017) observed also very similar that higher generation of heterogeneous oxidation occurs for semisolid particles compared to liquid particles. On a related note, Chim et al. (ACP, 17, 14415, 2017) found that fragmentation and volatilization processes play a larger role than the functionalization process in determining the evolution of aerosol water content and

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droplet size at high oxidation stages. These papers may be worth to discuss.

4. How exactly did you calculate model layer thicknesses? By reading L30 in P11, it appears that upon evaporation only the thickness of the sub-surface bulk layers are decreased, but not the thicknesses of the inner bulk, correct?

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