Atmospheric
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Supplement of

The oxidation regime and SOA composition in limonene ozonolysis: roles of different double bonds, radicals, and water

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The accuracy of particulate products analysis

For particulate products analysis, two factors that would impact the accuracy of the results were the deposition of gas-phase products on the filter and the volatilization of particle-phase products. To investigate the effect of the deposition of gas-phase products, after the first filter (PTFE or quartz filter) we added another filter (PTFE or quartz filter) to collect the gaseous products. Results showed that the products collected on the second filter were negligible meaning that the deposition of gas-phase species on filter did not have a great impact on the results. As for the effect of the volatilization of particle-phase products, the variation of SOA and particulate products yields on collection time was studied. The results showed that when the collection time was controlled to be 3 h the SOA loss caused by volatilization of particles was less than 6%, so the second factor was considered to have no obvious influence on the particulate products analysis.

The evolution of particulate total peroxides in solution

Figure S7 showed the time profiles of total peroxides evolution of SOA formed in different cases. Although the initial content of peroxides in particles was influenced by RH and OH scavenger, at each circumstance the variation of the total peroxides content with the storage time was similar. When SOA extract solution was stored at 277 K, the total peroxides concentration was found to decrease slightly, which was mainly attributed to the decay of some peroxides. The fact that the total peroxides content nearly maintained stable indicated that at 277 K some active components in particles would not go through obvious decay so that more uncertainty could be avoided. In addition, this phenomenon suggested that the H_2O_2 generation was due to the decomposition or hydration of some kinds of peroxides so the total peroxides concentration measured did not show large fluctuation.

The calculation equations

$$F_{Wall\ loss} = ([In] - [Out]) / [In] \qquad (S1)$$

Where $F_{Wall\ loss}$ is the wall loss fraction, [In] and [Out] are the inlet and outlet concentrations, respectively.

$$Y_i = \frac{N_i}{N_{lim}} \qquad (S2)$$

Where Y_i is the molar yield of product i, N_i (mol) is the number of moles of product i, and N_{lim} (mol) is

the number of moles of limonene reacted.

$$Y_{SCI} = Y_{H_2O_2-limit} + Y_{HMHP-limit} \qquad (S3)$$

Where Y_{SCI} is the molar yield of SCIs, $Y_{H2O2-limit}$ and $Y_{HMHP-limit}$ are the limiting molar yields of H_2O_2 and HMHP, respectively.

$$Y_{SOA} = \frac{M_{SOA}}{M_{lim}} \qquad (S4)$$

Where Y_{SOA} is the SOA yield, M_{SOA} ($\mu g\ m^{-3}$) is the aerosol mass concentration, and M_{lim} ($\mu g\ m^{-3}$) is the mass concentration of limonene reacted.

$$\omega = \frac{m_{peroxides}}{m_{SOA}} \qquad (S5)$$

Where ω is the mass fraction of particulate peroxides, $m_{peroxides}$ (μg) is the mass of particulate peroxides, and m_{SOA} (μg) is the mass of SOA.

The impact of the reactants concentrations

To get enough products for analysis in a short reaction time, both of the concentrations of limonene and ozone in this study were obviously higher than those in the real atmospheric conditions, which might have influence on the gas-phase and particle-phase chemistry. So the effects of the reactants concentrations on the experimental results are discussed below.

A major impact of the high concentrations of reactants is the increased RO_2 concentration. In recent years many studies reported that the autoxidation processes formed highly oxidized RO_2 radicals, which reacted with HO_2 and other RO_2 radicals forming highly oxidized multifunctional organic compounds (HOMs) (Jokinen et al., 2014; Richters et al., 2016a, b). The production of HOMs is controlled by two competing processes, i.e., RO_2 autoxidation vs. RO_2 reaction with HO_2 and other RO_2 radicals. Zhang et al. (2015) found that at low α-pinene levels, the longer lifetime of RO_2 radicals favored the isomerization pathways and consequently led to enhanced ELVOC dimers production. They estimated that the corresponding lifetime of RO_2 radicals decreased by less than an order of magnitude when the initial α-pinene mixing ratio increased from 10 ppbv to 150 ppbv, which was not sufficient to perturb the dynamics of overall RO_2 chemistry. In our experiments, where the limonene concentration was below 200 ppbv, we speculated that although the RO_2 chemistry was affected to some extent it would not bring huge influence on the results. When the RO_2 concentration is high, the reactions of SCIs and RO_2 radicals might happen in the system (Sadezky et al., 2008). Zhao et al. (2015) found that the reactions of SCIs and RO_2 radicals played a key role in particle formation in

trans-3-hexene ozonolysis, while for large alkenes such as terpenes and sesquiterpenes such reactions might be unimportant. Thus, although the concentrations of reactants used in this study were higher than that in the real atmospheric condition, the SCIs + RO_2 reactions did not have a huge impact on the reaction system. The SOA yield of limonene ozonolysis observed in this study was in the range of the values reported before (Ahmad et al., 2017; Chen and Hopke, 2010; Pathak et al., 2012). It is true that when the mixing ratios of reactants are high, the gas-particle partitioning processes of semi-volatility and low-volatility products are promoted resulting in higher SOA yield, yet we think that it may not have great impact on the representativeness of the products we investigated in particles.

Figure caption.

Figure S1. The diagram of the flow tube reactor

Figure S2. The diagram of the coil collector

Figure S3. The diagram of the Horibe tube

Figure S4. The dependence of peroxides wall loss fractions on relative humidity (RH). H_2O_2, hydrogen peroxide; HMHP, hydroxymethyl hydroperoxide; PFA, peroxyformic acid; PAA, peroxyacetic acid.

Figure S5. The dependence of carbonyls wall loss fractions on relative humidity (RH). HACE, hydroxyacetone; FA, formaldehyde; AA, acetaldehyde; ACE, acetone; GL, glyoxal; MGL, methylglyoxal.

Figure S6. The dependence of SOA wall loss fractions on relative humidity (RH).

Figure S7. Time profiles of total peroxides evolution per particle mass of different SOA formed (a) without OH scavenger, (b) with 2-butanol, and (c) with cyclohexane in the relative humidity (RH) range of 0%–90% at high $[O_3]/[limonene]$.

Figure S8. The variation of the molar fraction of unstable peroxides in particles with relative humidity (RH) at low or high $[O_3]/[limonene]$ in the presence or absence of OH scavenger (2-butanol or cyclohexane).

Figure S9. The variation of high-molecule-weight peroxides molar yields with relative humidity (RH) at low or high $[O_3]/[limonene]$ in the presence or absence of OH scavenger (2-butanol or cyclohexane).

Figure S10. Dependence of formaldehyde yield on relative humidity (RH) at low or high $[O_3]/[limonene]$ in the presence or absence of OH scavenger (2-butanol or cyclohexane).

References

Ahmad, W., Coeur, C., Cuisset, A., Coddeville, P., and Tomas, A.: Effects of scavengers of Criegee intermediates and OH radicals on the formation of secondary organic aerosol in the ozonolysis of limonene, J. Aerosol Sci., 110, 70–83, doi: 10.1016/j.jaerosci.2017.05.010, 2017.

Chen, X., and Hopke, P. K.: A chamber study of secondary organic aerosol formation by limonene ozonolysis, Indoor Air, 20, 320–328, doi: 10.1111/j.1600-0668.2010.00656.x, 2010.

Jokinen, T., Sipilä, M., Richters, S., Kerminen, V. M., Paasonen, P., Stratmann, F., Worsnop, D., Kulmala, M., Ehn, M., Herrmann, H., and Berndt, T.: Rapid autoxidation forms highly oxidized RO_2 radicals in the atmosphere, Angew. Chem. Int. Ed., 53, 14596–14600, doi: 10.1002/anie.201408566, 2014.

Pathak, R. K., Salo, K., Emanuelsson, E. U., Cai, C., Lutz, A., Hallquist, A. M., and Hallquist, M.: Influence of ozone and radical chemistry on limonene organic aerosol production and thermal characteristics, Environ. Sci. Technol., 46, 11660–11669, doi: 10.1021/es301750r, 2012.

Richters, S., Herrmann, H., and Berndt, T.: Different pathways of the formation of highly oxidized multifunctional organic compounds (HOMs) from the gas-phase ozonolysis of β-caryophyllene, Atmos. Chem. Phys., 16, 9831−9845, doi: 10.5194/acp-16-9831-2016, 2016a.

Richters, S., Herrmann, H., and Berndt, T.: Highly oxidized RO_2 radicals and consecutive products from the ozonolysis of three-sesquiterpenes, Environ. Sci. Technol., Environ. Sci. Technol., 50, 2354−2362, doi: 10.1021/acs.est.5b05321, 2016b.

Sadezky, A., Winterhalter, R., Kanawati, B., Römpp, A., Spengler, B., Mellouki, A., Le Bras, G., Chaimbault, P., and Moortgat, G. K.: Oligomer formation during gas-phase ozonolysis of small alkenes and enol ethers: new evidence for the central role of the Criegee intermediate as oligomer chain unit, Atmos. Chem. Phys., 8, 2667–2699, doi:10.5194/acp-8-2667-2008, 2008.

Zhao, Y., Wingen, L. M., Perraud, V., Greaves, J., and Finlayson-Pitts, B. J.: Role of the reaction of stabilized Criegee intermediates with peroxy radicals in particle formation and growth in air, Phys. Chem. Chem. Phys., 17, 12500–12514, doi:10.1039/C5CP01171J, 2015.

Zhang, X., McVay, R. C., Huang, D. D., Dalleska, N. F., Aumont, B., Flagan, R. C., and Seinfeld, J. H.: Formation and evolution of molecular products in α-pinene secondary organic aerosol, Proc. Natl. Acad. Sci., 112, 14168–14173, doi: 10.1073/pnas.1517742112, 2015.

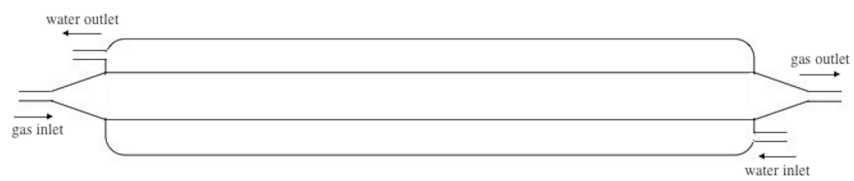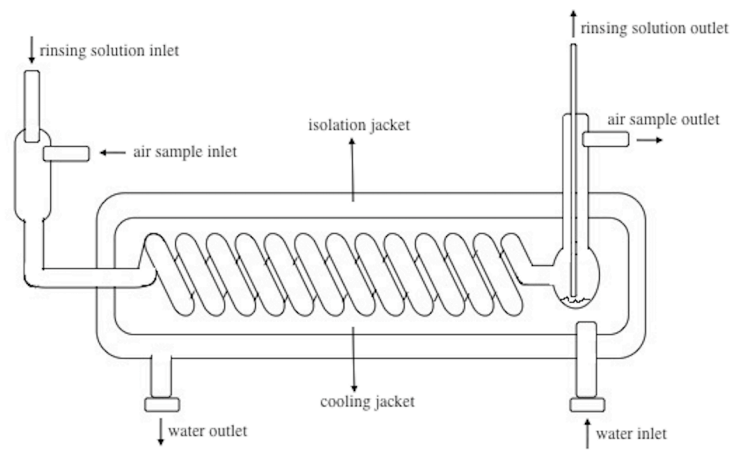**Figure S1.** The diagram of the flow tube reactor

rinsing solution inlet

rinsing solution outlet

isolation jacket

air sample outlet

air sample inlet

cooling jacket

water outlet

water inlet

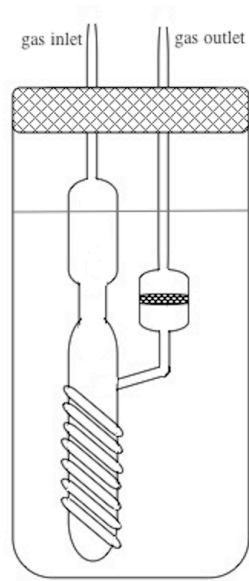**Figure S2.** The diagram of the coil collector
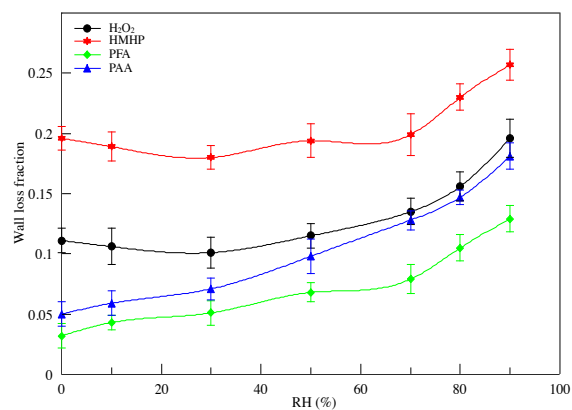
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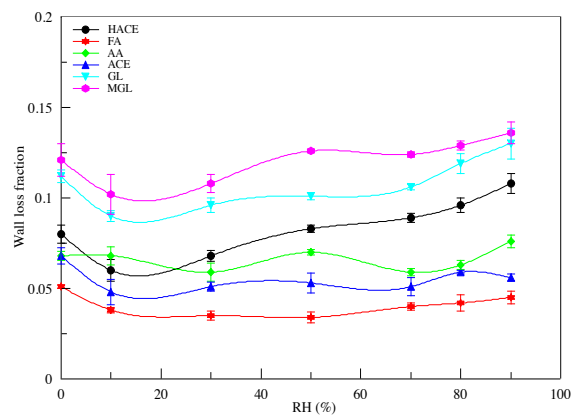
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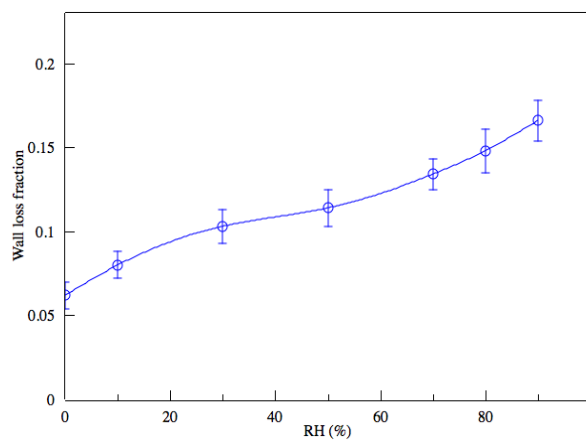
Figure S6. The dependence of SOA wall loss fractions on relative humidity (RH).
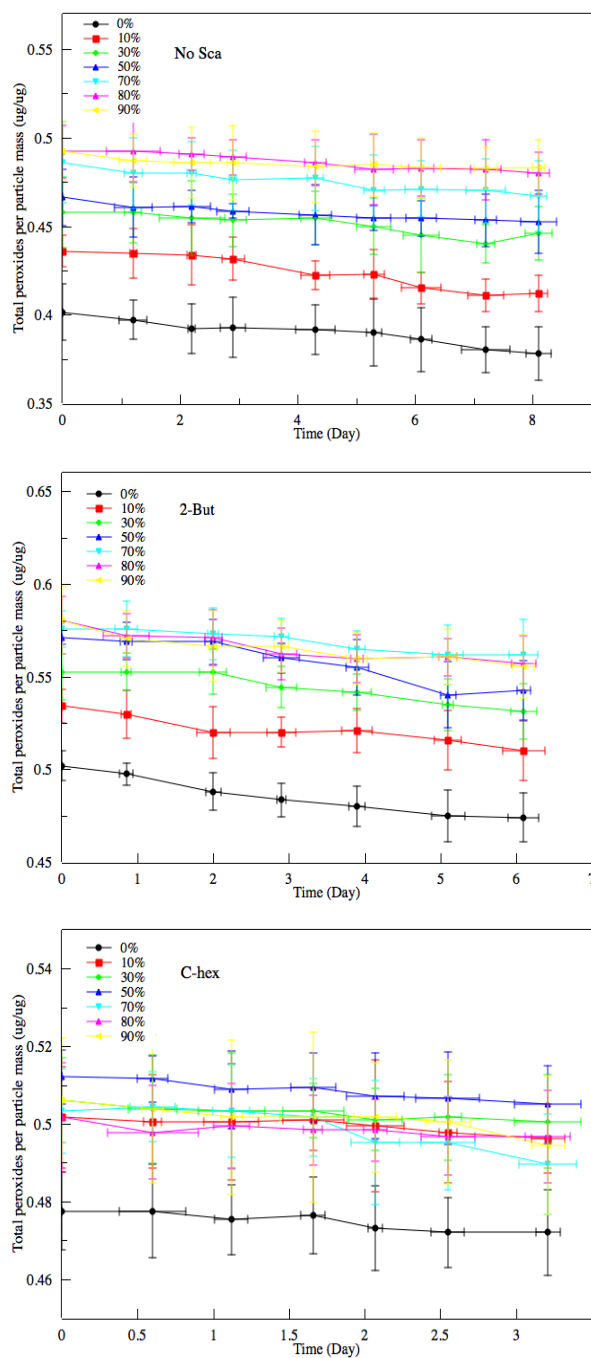
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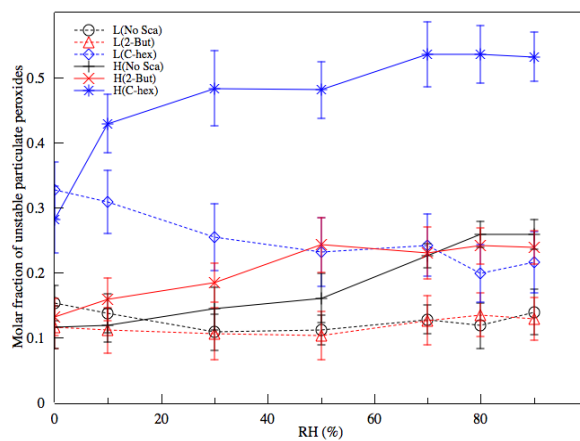
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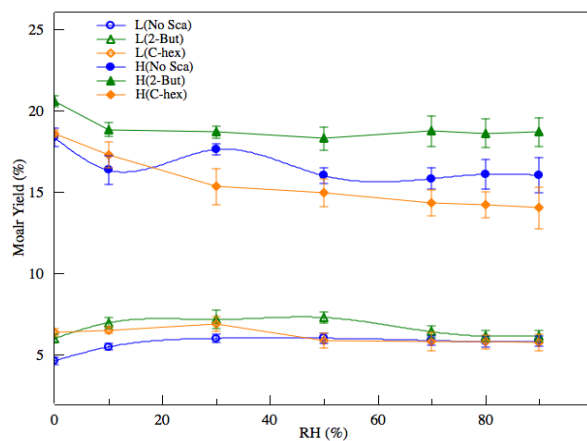
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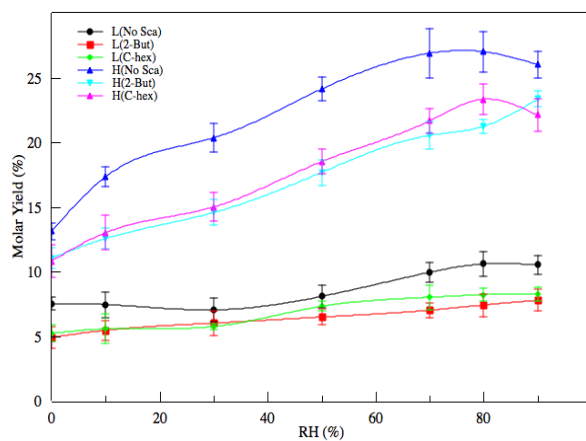
Figure S10. Dependence of formaldehyde yield on relative humidity (RH) at low or high [O_3]/[limonene] in the presence or absence of OH scavenger (2-butanol or cyclohexane).