November 16, 2020

ACP Editor

Dear Prof. Nga Lee Ng,

Enclosed please find our revised manuscript entitled "***Quantification of the role of stabilized Criegee intermediates in the formation of aerosols in limonene ozonolysis***", revised supplement and two responses to the anonymous referees #1 and #2. We gratefully appreciate the reviewers for their constructive suggestions to help us improve the manuscript. We revised the manuscript by responding to all comments point by point. We sincerely hope the revised manuscript is suitable for publication on ACP.

The major revisions are specified as follows:

1. The effect of 2-butanol on SCIs reactions was revaluated in the revised manuscript, and the experiments with cyclohexane as OH scavenger were conducted.

2. Discussion on the effect of aerosols acidity on the results was added in the manuscript.

3. Details on the formation and measurement of H_2O_2 were added in the Supplement.

4. Discussion on the effect of the reactants concentrations on the results has been added in the Supplement.

Detailed changes made in the manuscript can be seen in the marked-up version in this response.

Thanks for your time.

Sincerely yours,

Zhongming Chen and Yiwei Gong

Response to Reviewer #1

We gratefully thank you for your constructive comments and through review. Below are our point-by-point responses to your comments.

(Q=Question, A= Answer, C=Change in the revised manuscript)

General Comments: Gong and Chen report the experimental study on the formation of SOA during the ozonolysis of limonene, a class of important biogenic VOC in the atmosphere. They used flow tube reactors under different relative humidity (RH) to investigate the mechanism of SOA formation, especially the role of stabilized Criegee intermediates (SCIs). Their findings imply the different mechanisms of SOA formation at dry vs humid condition. The subject is within the scope of ACP and some findings seem important from the viewpoint of atmospheric aerosol chemistry. However, I am concerned about some critical issues that should be addressed.

A: We highly appreciate your comments and suggestions. The questions you mentioned are answered as follows.

Specific Comments:

Q1. I am most concerned about the side reaction of SCIs with 2- butanol. In page 10, the authors wrote "The rate constants of CH2OO reaction with methanol and ethanol were measured to be about 10ˆ−15 cm3 molecule−1 s−1 at 298 K (McGillen et al., 2017)", but this statement is incorrect. Actually, McGillen et al. (ACS Earth Space Chem. 2017, 1, 664−672) experimentally determined the rate constants k ~ 10ˆ-13 cm3 molecule−1 s−1 for CH2OO + CH3OH/C2H5OH and k ~ 4 x 10ˆ-14 cm3 molecule−1 s−1 for (CH3)2COO + CH3OH at ~ 298 K. Furthermore, Tadayon et al. (J. Phys. Chem. A 2018, 122, 1, 258–268) reported the rate constants of (1.9 ± 0.5) × 10ˆ–13 cm3 molecule-1 s–1 for the reaction of CH2OO with 2-propanol at 295 K. Hence, the assumption that the rate constant of limonene-derived SCIs reaction with 2-butanol is 10ˆ−15 cm3 molecule−1 s−1 seems to be inadequate. If the authors assumed the rate constant to be 10ˆ−13 cm3 molecule−1 s−1, then the ratio of the amount of SCIs reacted with 2-butanol to the amount of SCIs reacted with AA would be much larger than the value authors claimed. Thus, SCIs in the presence of an excess amount of 2-butanol would be exclusively converted into alpha-alkoxyalkyl-hydroperoxides, that may contribute to the observed SOA formation. The authors should discuss the issue for details.

A1: Thanks for your suggestion and we regret that we did not calculate the impact of adding 2-butanol correctly. We have revaluated the effect of 2-butanol on SCIs reactions in the revised manuscript, and to better understand the structure-dependent reactivity of SCIs, the chemical structures of SCIs formed from endo-DB and exo-DB ozonolysis are provided in the Supplement. Besides, we also conducted experiments with cyclohexane and lower concentration of 2-butanol to confirm the impact of 2-butanol.

C1: Lines 307–331 in Sect. 3.3.2:

Previous studies reported that as for the reactions of SCIs with alcohols, the substitution group of alcohols had little effect on the reactions, while the structures of SCIs showed an obvious influence. The rate constants of CH_2OO reaction with alcohols were about 10^{-13} cm^3 $molecule^{-1}$ s^{-1} at 298 K (Tadayon et al., 2018), and it was slower for $(CH_3)_2COO$ reaction with alcohols, whose rate constants were reported to be 10^{-15} ~ 10^{-14} cm^3 $molecule^{-1}$ s^{-1} (Aroeira et al., 2019; McGillen et al., 2017). Watson et al. (2019) computed that the rate constant of *syn*-CH_3CHOO + CH_3OH was about 10^{-17} cm^3 $molecule^{-1}$ s^{-1}, which was much smaller than that of about 10^{-12} cm^3 $molecule^{-1}$ s^{-1} for *anti*-CH_3CHOO + CH_3OH at 298 K. In limonene ozonolysis, several kinds of SCIs were produced and their structures were shown in Fig. S7. A mono-substituted SCIs and a di-substituted SCIs were formed from endo-DB ozonolysis, and exo-DB ozonolysis produced CH_2OO and a di-substituted SCIs. When assuming the rate constant of SCIs reaction with 2-butanol as 10^{-14} cm^3 $molecule^{-1}$ s^{-1}, it was estimated that in terms of the concentrations of AA used in experiments, the ratio of the amount of SCIs reacted with 2-butanol to the amount of SCIs reacted with AA ranged from 0.06 to 1.25, and this ratio might be higher in exo-DB oxidation because of the formation of CH_2OO. This meant that part of SCIs could react with 2-butanol, producing α-alkoxyalkyl-hydroperoxides and contributing to the observed SOA, especially when using low concentrations of AA and water. To figure out whether the SOA formation potentials of SCIs estimated here were higher than those under the situation without 2-butanol, the experiments with cyclohexane as OH scavenger were carried out, and the details were described in the Supplement. It was found that with the use of cyclohexane, SCIs reactions still accounted for more than 60% in SOA formation and according to the fitting results, the SOA formation potentials of SCIs were even a bit larger than those with the use of 2-butanol, and their deviations were within 12%. This phenomenon was speculated to be due to the higher concentration of RO_2 radicals when using cyclohexane, promoting the reactions of SCIs with RO_2. To further determine the impact of 2-butanol, we also conducted experiments with the concentration of 2-butanol as about 150 ppmv, which was half of the previous concentration of 2-butanol used in experiments and was estimated to be sufficient for scavenging more than 99% OH radicals. It was observed that the amount of SOA formation was not impacted by the concentration of 2-butanol, and the SOA formation potentials of SCIs under a lower concentration of 2-butanol were similar with those under a higher concentration of 2-butanol. Based on the results elaborated above, we confirmed that the effect of 2-butanol on the results was limited.

Q2. Adding AA and water (increasing relative humidity) should change the acidity of SOA. It is known that the pH dramatically influences the fates of ozonation products in condensed phase. See Zhao et al. J. Phys. Chem. A 2018, 122, 5190 and Qiu et al. Environ. Sci. Technol. 2020, doi.org/10.1021/acs.est.0c03438 for example. How does the change of SOA acidity influence the results?

A2: Thanks for your suggestion. The acidity of aerosols is an issue needing consideration and we have added a discussion on the effect of SOA acidity on the results in the revised manuscript.

C2: Lines 344–361 in Sect. 3.3.3:

In this study, with the addition of AA the acidity of aerosols would change, and some reactions that happened in bulk phase were influenced, especially under high-humidity conditions. In view of this, the effect of SOA acidity on particle-phase reactions was considered. Zhao et al. (2018) investigated the aqueous-phase hydrolysis of α-acyloxyalkyl-hydroperoxides, which were produced from reactions of SCIs and organic acids. It was found that α-acyloxyalkyl-hydroperoxides decomposed promptly when pH was larger than 5 in aqueous phase. The aqueous decomposition of α-hydroxyalkyl-hydroperoxides was also reported to be accelerated by acids, and the rate coefficients of decay increased with decreasing pH (Qiu et al., 2020a). These studies implied that acids, acting as catalysts, promoted the decomposition processes of some compounds in liquid particles and might reduce the amount of SOA. However, the effect of acidity on bulk-phase reactions was found to be complicated, and Iinuma et al. (2004) reported that acidity promoted the formation of large molecules in particles. Some reactions, which produced peroxyacetals, esters, aldols, etc., and contributed to SOA formation, could be catalyzed by acids and H^+ in aqueous phase (Ziemann and Atkinson, 2012), while the rate coefficients of these reactions with varying pH were not clear. Actually, we could not evaluate the effect of acidity on the formation of SOA accurately because the acidity of aerosols might impact a series of reactions, and the mechanisms and rates of these reactions at different pH were vague. It was noted that Chen et al. (2008) found that in the aqueous-phase ozonolysis of methacrolein and methyl vinyl ketone, the yields of products were almost independent of pH, and Zhang et al. (2009) also observed this phenomenon in the ozonolysis of α-pinene and β-pinene in aqueous phase. Thus the effect of the particle acidity on the results might also be limited here, and the accurate estimates of this issue still needed further research.

Q3. It has been reported that water accelerates the decomposition of alpha-hydroxyalkyl-hydroperoxides (formed by SCIs + water) and alpha-acyloxy-hydroperoxides (formed by SCIs + carboxylic acids) [see Zhao et al. J. Phys. Chem. A 2018, 122, 5190, Qiu et al. Environ. Sci. Technol. 2020, 54, 3890−3899]. Could this humidity-assisted decomposition of ROOH explain the observed RH effects on SOA yield? The authors should comment on the issue in the text.

A3: Thanks for your suggestion. Water could accelerate the decomposition processes of α-acyloxyalkyl-hydroperoxides and α-hydroxyalkyl-hydroperoxides in aqueous phase, resulting in the formation of H_2O_2. The reactions of H_2O_2 in particles have been thought to be important and may impact the aerosols formation. A discussion about this issue was provided in the revised manuscript.

C3: Lines 368–377 in Sect. 3.3.3:

On the other hand, a significant amount of H_2O_2 formed from SCIs reaction with water was observed in ozonolysis under high-humidity conditions (Chen et al., 2016; Jiang et al., 2013), and water was reported to accelerate the decomposition of α-acyloxyalkyl-hydroperoxides and α-hydroxyalkyl-hydroperoxides in aqueous phase, resulting in the formation of H_2O_2 (Qiu et al., 2019, 2020b; Zhao et al., 2018). H_2O_2 was reported to play an important role in the nonradical oxidation of carbonyls in aqueous phase (Galloway et al., 2011; Herrmann et al., 2015), producing hydroxyhydroperoxides and promoting SOA formation (Zhao et al., 2012, 2013). The H_2O_2 oxidation of carbonyls was speculated to mainly occur in surface liquid layer of aerosols, resulting in the generation of organic peroxides and high-molecular-weight oligomers (Sui et al., 2017; Zhang et al., 2019). The impact of H_2O_2 reactions at air-liquid interface might be another reason for the performances of SCIs in SOA formation under high-humidity conditions.

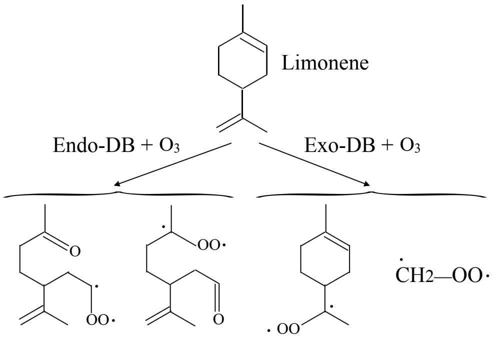


Figure S7. Structures of limonene-derived SCIs formed from endo-DB and exo-DB ozonolysis.

References

Aroeira, G. J. R., Abbott, A. S., Elliott, S. N., Turney, J. M., and Schaefer III, H. F.: The addition of methanol to Criegee intermediates, Phys. Chem. Chem. Phys., 21, 17760−17771, doi: 10.1039/C9CP03480C, 2019.

Chen, L., Wang, W. L., Wang, W. N., Liu, Y. L., Liu, F. Y., Liu, N., and Wang, B. Z.: Water-catalyzed decomposition of the simplest Criegee intermediate CH_2OO, Theor. Chem. Acc., 135, 131, doi: 10.1007/s00214-016-1894-9, 2016.

Chen, Z. M., Wang, H. L., Zhu, L. H., Wang, C. X., Jie, C. Y., and Hua, W.: Aqueous-phase ozonolysis of methacrolein and methyl vinyl ketone: a potentially important source of atmospheric aqueous oxidants, Atmos. Chem. Phys., 8, 2255–2265, doi: 10.5194/acp-8-2255-2008, 2008.

Galloway, M. M., Loza, C. L., Chhabra, P. S., Chan, A. W. H., Yee, L. D. Seinfeld, J. H., and Keutsch, F. N.: Analysis of photochemical and dark glyoxal uptake: implications for SOA formation, Geophys. Res. Lett., 38, L17811, doi: 10.1029/2011GL048514, 2011.

Herrmann, H., Schaefer, T., Tilgner, A., Styler, S. A., Weller, C., Teich, M., and Otto, T.: Tropospheric aqueous-phase chemistry: kinetics, mechanisms, and its coupling to a changing gas phase, Chem. Rev., 115, 4259–4334, doi: 10.1021/cr500447k, 2015.

Iinuma, Y., Böge, O., Gnauk, T., and Herrmann, H.: Aerosol-chamber study of the α-pinene/O_3 reaction: influence of particle acidity on aerosol yields and products, Atmos. Environ., 38, 761–773, doi: 10.1016/j.atmosenv.2003.10.015, 2004.

Jiang, L., Lan, R., Xu, Y. S., Zhang, W. J., and Yang, W.: Reaction of stabilized Criegee intermediates from ozonolysis of limonene with water: Ab Initio and DFT study, Int. J. Mol. Sci., 14, 5784–5805, doi: 10.3390/ijms14035784, 2013.

McGillen, M. R., Curchod, B. F. E., Chhantyal-Pun, R., Beames, J. M., Watson, N., Khan, M. A. H., McMahon, L., Shallcross, D. E., and Oee-Ewing, A. J.: Criegee intermediate−alcohol reactions, a potential source of functionalized hydroperoxides in the atmosphere, ACS Earth Space Chem., 1, 664−672, doi: 10.1021/acsearthspacechem.7b00108, 2017.

Qiu, J. T., Ishizuka, S., Tonokura, K., Colussi, A., and Enami, S.: Water dramatically accelerates the decomposition of α-hydroxyalkyl-hydroperoxides in aerosol particles, J. Phys. Chem. Lett., 10, 5748−5755, doi: 10.1021/acs.jpclett.9b01953, 2019.

Qiu, J. T., Tonokura, K., and Enami, S.: Proton-catalyzed decomposition of α-hydroxyalkyl-hydroperoxides in water, Environ. Sci. Technol., 54, 10561–10569, doi: 10.1021/acs.est.0c03438, 2020a.

Qiu, J. T., Liang, Z. C., Tonokura, K., Colussi, A. J., and Enami, S.: Stability of monoterpene-derived α-hydroxyalkyl-hydroperoxides in aqueous organic media: relevance to the fate of hydroperoxides in aerosol particle phases, Environ. Sci. Technol., 54, 3890−3899, doi: 10.1021/acs.est.9b07497, 2020b.

Sui, X., Zhou, Y. F., Zhang, F., Chen, J. M., Zhu, Z. H., and Yu, X. Y.: Deciphering the aqueous chemistry of glyoxal oxidation with hydrogen peroxide using molecular imaging, Phys. Chem. Chem. Phys., 19, 20357–20366, doi: 10.1039/C7CP02071F, 2017.

Tadayon, S. V., Foreman, E. S., and Murray, C.: Kinetics of the reactions between the Criegee intermediate CH_2OO and alcohols, J. Phys. Chem. A, 122, 258−268, doi: 10.1021/acs.jpca.7b09773, 2018.

Watson, N. A. I., Black, J. A., Stonelake, T. M., Knowles, P. J., and Beames, J. M.: An extended computational study of Criegee intermediate−alcohol reactions, J. Phys. Chem. A, 123, 218−229, doi: 10.1021/acs.jpca.8b09349, 2019.

Zhang, F., Yu, X. F., Chen, J. M., Zhu, Z. H., and Yu, X. Y.: Dark air–liquid interfacial chemistry of glyoxal and hydrogen peroxide, NPJ Clim. Atmos. Sci., 2, 28, doi: 10.1038/s41612-019-0085-5, 2019.

Zhang, X., Chen, Z. M., Wang, H. L., He, S. Z., and Huang, D. M.: An important pathway for ozonolysis of alpha-pinene and beta-pinene in aqueous phase and its atmospheric implications, 43, 4456–4471, doi: 10.1016/j.atmosenv.2009.06.028, 2009.

Zhao, R., Lee, A. K. Y., and Abbatt, J. P. D.: Investigation of aqueous-phase photooxidation of glyoxal and methylglyoxal by aerosol chemical ionization mass spectrometry: observation of hydroxyhydroperoxide formation, J. Phys. Chem. A, 116, 6253–6263, doi: 10.1021/jp211528d, 2012.

Zhao, R., Lee, A. K. Y., Soong, R., Simpson, A. J., and Abbatt, J. P. D.: Formation of aqueous-phase alpha-hydroxyhydroperoxides (α-HHP): potential atmospheric impacts, Atmos. Chem. Phys., 13, 5857–5872, doi: 10.5194/acp-13-5857-2013, 2013.

Zhao, R., Kenseth, C. M., Huang, Y. L., Dalleska, N. F., Kuang, X. M., Chen, J. R., Paulson, S. E., and Seinfeld, J. H.: Rapid aqueous-phase hydrolysis of ester hydroperoxides arising from Criegee intermediates and organic acids, J. Phys. Chem. A, 122, 5190−5201, doi: 10.1021/acs.jpca.8b02195, 2018.

Ziemann, P. J. and Atkinson, R.: Kinetics, products, and mechanisms of secondary organic aerosol formation, Chem. Soc. Rev., 41, 6582–6605, doi: 10.1039/c2cs35122f, 2012.

Response to Reviewer #2

We gratefully thank you for your constructive comments and through review. Below are our point-by-point responses to your comments.

(Q=Question, A= Answer, C=Change in the revised manuscript)

General Comments: This manuscript by Gong and Chen describes a series of laboratory experiments, aiming to elucidate the contribution of stabilized Criegee intermediates (SCIs) to the formation of SOA from limonene. The authors used a creative flow tube setup to investigate SCIs arising from ozonation of the endo- and exo-double bonds (DBs) separately. By employing an SCI scavenger in the system, the authors claimed that they have quantified the contribution of SCI chemistry towards the SOA yields as a function of RH. The major conclusion is that water plays a complex role in the reaction system, suppressing SOA formation under low RH, while facilitating SOA formation at high RH. Over the past few years, the importance of SCI chemistry in the atmosphere has become evident. With SCI being a reactive intermediate that is difficult to detect, quantitative evaluations for the importance of SCI is lacking. This manuscript aims to provide quantitative information that fills our gap in understanding. The topic is timely and is within the scope of ACP. The writing and data analyses were conducted with caution. However, I have concerns regarding a few approaches and assumptions that authors employ in the study. I recommend a major revision before publication on ACP.

A: We highly appreciate your comments and suggestions. The questions you mentioned are answered as follows.

Major comments:

Q1. I'm afraid that the contribution of SCI to the SOA formation may be exaggerated in the current setup due to the presence of a high concentration of butanol (OH scavenger). The authors provided an estimate that 12.5% of SCI has reacted with butanol, using a lower-band estimate for the SCI reactivity with alcohol. It is not convincing that the effect of butanol is "not important (Line 304)". Can the author perform an experiment with an aprotic OH scavenger (e.g., hexane) to experimentally confirm their assumption?

A1: Thanks for your suggestion. Here to evaluate whether the addition of 2-butanol made obvious impacts on the results, we conducted experiments with cyclohexane as OH scavenger, and the results were discussed as follows.

Part of SCIs might react with 2-butanol, producing α-alkoxyalkyl-hydroperoxides and contributing to the observed SOA, especially when using low concentrations of AA and water. To figure out whether the SOA formation potentials of SCIs estimated here were higher than those under the situation without 2-butanol, the experiments with cyclohexane as OH scavenger were carried out. Here three representative conditions: dry conditions, 40% RH (representing low-humidity conditions) and 80% RH (representing high-humidity conditions), were analyzed in the endo-DB ozonolysis. The abilities of 2-butanol and cyclohexane on scavenging OH radicals were similar (Chew and Atkinson, 1996), however, the use of different OH scavengers brought different impacts on the reaction system. When 2-butanol was used, higher $[HO_2]/[RO_2]$ was observed, which was thought to be more similar to the atmospheric conditions, while adding cyclohexane resulted in a lower $[HO_2]/[RO_2]$ (Docherty and Ziemann, 2003; Jonsson et al., 2008). In view of this, this study chose 2-butanol as OH scavenger, while the use of cyclohexane could provide a contrast to help us better understand the mechanisms in the reaction system.

In the experiments with cyclohexane, the concentrations of limonene and O_3 were about 90 ppbv and 270 ppbv, and the reaction time was 240 s. Around 400 ppmv of cyclohexane was added to scavenge OH radicals. With the addition of cyclohexane, the SOA yields were found to be lower than those with the addition of 2-butanol, suggesting that higher concentration of HO_2 radicals promoted aerosols formation (Keywood et al., 2004). Through adding different concentrations of AA (24–480 ppbv), the amount of SCIs in the reaction system was regulated and calculated as elaborated in Sect. 3.1, and the dependence of SOA mass concentration on the amount of SCIs was shown in Fig. S8. The SCIs reactions still accounted for more than 60% in SOA formation and according to the fitting results, the SOA formation potentials of SCIs under the use of cyclohexane were even a bit larger than those under the use of 2-butanol, and the deviations were within 12%. This phenomenon was speculated to be due to the higher concentration of RO_2 radicals when using cyclohexane, promoting the reactions of SCIs with RO_2.

To further determine the impact of 2-butanol, we also conducted experiments with the concentration of 2-butanol as about 150 ppmv, which was half of the previous concentration of 2-butanol used in experiments and was estimated to be sufficient for scavenging more than 99% OH radicals. It was observed that the amount of SOA formation was not impacted by the concentration of 2-butanol, and the SOA formation potentials of SCIs under a lower concentration of 2-butanol were similar with those under a higher concentration of 2-butanol. Based on the results elaborated above, we confirmed that the effect of 2-butanol on the results was limited. We have added the details on the experiments with cyclohexane in the Supplement.

Q2. The fraction of SCI reacting with water (SCI_I) was estimated solely from the formation of H_2O_2.

- How did the authors measure H_2O_2? Was it the gas phase H_2O_2 or particle phase?

- Although I agree that H_2O_2 is the major decomposition product of α-hydroxyhydroperoxides (product of SCI + H_2O), the decomposition of α-hydroxyhydroperoxides is an equilibrium process and may not always proceed completely.

- α-hydroxyhydroperoxides are not the only source of H_2O_2. It's known that H_2O_2 is generated in SOA extracts, likely due to the decomposition of larger organic peroxides.

- In particular, Zhao et al. 2018, J. Phys. Chem. A reported H_2O_2 arising from the decomposition of hydroperoxyester, which is formed from SCI + organic acids. Although the mechanism is not completely clear, this implies that the product of SCI + AA may also give rise to H_2O_2.

Citation: Ran Zhao, Christopher M. Kenseth, Yuanlong Huang, Nathan F. Dalleska, Xiaobi M. Kuang, Jierou Chen, Suzanne E. Paulson, and John H. Seinfeld, The Journal of Physical Chemistry A 2018 122 (23), 5190-5201 DOI: 10.1021/acs.jpca.8b02195

A2: Thanks for your suggestions. When we estimated the yield of SCI_I in limonene ozonolysis, the formation of gas-phase H_2O_2 was measured, which was elaborated in our previous study (Gong et al., 2018). For the detection of gas-phase H_2O_2, the gas samples passing through the PTFE filter were collected in a glass coil collector at a temperature of 4 °C with H_3PO_4 solution (pH 3.5) serving as the rinsing solution. After the collection, solutions containing peroxides were analyzed by HPLC (Agilent 1100, USA) coupled with post-column derivatization and fluorescence detection online. Peroxides separated by column chromatography reacted with *p*-hydroxyphenylacetic acid (POPHA) to form POPHA dimers under the catalysis of hemin, and then the dimers were quantified using a fluorescence detector. With the increase of RH, it was observed that the yield of H_2O_2 increased significantly from dry conditions to 70% RH, and the H_2O_2 yield approached the limiting value above 70% RH, suggesting that reaction with water suppressed other reactions of SCI_I. In the exo-DB oxidation, the formation of hydroxymethyl hydroperoxide was also taken into consideration. Through the box model simulation, the contribution of HO_2 self-reaction to H_2O_2 formation was estimated to be limited. As for the reaction of SCIs with water, the products α-hydroxyalkyl hydroperoxides were reported to be preferential to decompose and generate H_2O_2 (Chen et al., 2016; Kumar et al., 2014). Although theoretical calculations indicated that the decomposition of α-hydroxyalkyl hydroperoxides was slow, some studies proved that water and acids could significantly catalyze the process (Anglada et al., 2002, 2011; Aplincourt and Anglada, 2003; Crehuet et al., 2001), and H_2O_2

formation occurred rapidly (Chen et al., 2016; Winterhalter et al., 2000). In addition, few α-hydroxyalkyl hydroperoxides larger than hydroxymethyl hydroperoxide were identified in gas phase, and the decomposition of α-hydroxyalkyl hydroperoxides was speculated to be totally completed.

The generation of H_2O_2 from aerosols in aqueous phase, which is mainly due to the decomposition of some compounds, has received attentions in recent years (Wang et al., 2011; Zhao et al., 2018). Here only the gas-phase H_2O_2 was detected to estimate the yield of SCI_I, while it was still needed to analyze whether the formation of H_2O_2 in SOA could impact the results. Zhao et al. (2018) reported the aqueous decomposition rate coefficients of α-acyloxyalkyl hydroperoxides, whose lifetime was estimated to be about 24 min in liquid aerosols. As the reaction time in flow tube reactors was around 4 min, the H_2O_2 formation from aerosols was not considered to contribute much to gas-phase H_2O_2 in this study. In addition, it was found that the dependence of H_2O_2 yield on RH could be well simulated with the gas-phase mechanisms, confirming that the particle-phase formation of H_2O_2 did not make obvious impact on the results. We have added the discussion about the formation and measurement of H_2O_2 in the Supplement.

Q3. The flow tube experiments employ tens of ppb of limonene with an excess amount of O_3 for reactions. While these concentrations are rather typical for flow tube experiments, I think the author should discuss the feasibility of extrapolating their flow tube results to the real environment. As the authors point out, limonene mixing ratios are at the sub-ppb level for forest and urban environments. In my opinion, SCIs will predominantly react with water when organic concentrations are low. Thus, the SOA formation potential of SCIs they determine in the flow tube may or may not be applicable to the ambient conditions.

A3: Thanks for your suggestion and a discussion on the effect of the concentrations of reactants has been added in the Supplement. In this study, to get enough products for analysis in a short reaction time, both of the concentrations of limonene and O_3 used in experiments were higher than those in the real atmosphere, and it was needed to consider the effect of concentrations of reactants. In the atmosphere, the concentrations of organic compounds formed from limonene ozonolysis are much smaller than those in flow tube reactors, while it should be noted that limonene-derived SCIs would not only react with the compounds formed from limonene, they could also react with other compounds in the ambient air. In this study, we determined the rate of SCIs isomerization and reaction with other products. In the atmosphere, the organic compounds that SCIs could react with are generally carboxylic acids, carbonyls, alcohols, and RO_2 radicals, and the concentrations of these compounds in forest are about 10^{11} molecule cm^{-3}, 10^{11} molecule cm^{-3}, 10^{11} molecule cm^{-3}, and 10^9 molecule

cm^{-3}, respectively. In urban area, the concentrations of carbonyls and alcohols were reported to be higher because of the anthropogenic emissions (Vereecken et al., 2012). The rate coefficients of SCIs reaction with carboxylic acids, carbonyls, alcohols, and RO_2 radicals were reported to be around 10^{-10} molecule cm^3 s^{-1}, 10^{-12} molecule cm^3 s^{-1}, 10^{-14} molecule cm^3 s^{-1}, and 10^{-11} molecule cm^3 s^{-1}, respectively (Khan et al., 2018; Lin and Chao, 2017; Zhao et al., 2017). It was estimated that the sum of the rate of SCIs isomerization and reaction with organic compounds in the atmosphere was on the same order of magnitude as that in experiments, and thus the results obtained here were considered to be feasible to the ambient conditions. We declare that further studies on different concentrations of reactants with the coexistence of other organic compounds would make the results more concise.

Minor and Technical Comments:

Q4. Line 155 “that” to “than”

A4: We have revised that.

Q5. Line 307 the sentence: “The reactions of SCIs with the compounds formed from SCIs scavengers would not compensate the effect of the consumption of SCIs on SOA formation.” is unclear. Please rephrase.

A5: Thanks for your suggestion. We have revised this sentence as follows.

C5: Lines 335–336 in Sect. 3.3.2:

The major role of SCIs scavengers was consuming SCIs in the reaction system, and the effect of products formed from SCIs scavengers on SCIs reactions was not expected to be important.

Q6. I’m supportive of the authors’ idea to provide an atmospheric implication of their findings by simulating three scenarios: forest, urban, and indoor. Instead of investigating all the RH for each scenario, I wonder if authors can constrain the RH to ranges that are more relevant to each scenario? For instance, the most comfortable RH range for human occupancy in an indoor environment is between 30 to 60%. It is unlikely we see an indoor that are extremely dry or wet.

A6: Thanks for your suggestion. The relevant RH under each scenario was considered and provided in the revised manuscript.

C6: Lines 413–418 in Sect. 3.4:

In forest, the typical RH is higher than 60%, and for urban and indoor area, they are usually under low-humidity conditions (Carslaw, 2017; Vereecken et al., 2012). According to the SOA formation potential of SCIs, it is estimated that the typical contribution of limonene-derived SCIs to SOA formation is $(8.21 \pm 0.15) \times 10^{-2}$ μg m^{-3} h^{-1} in forest, $(4.26 \pm 0.46) \times 10^{-2}$ μg m^{-3} h^{-1} in urban area, and $(2.52 \pm 0.28) \times 10^{-1}$ μg m^{-3} h^{-1} in indoor area.

Q7. Acid anhydrides can be hydrolyzed to form organic acids. By any chance, can the acid anhydrides arising from SCI + AA be hydrolyzed at higher RH, regenerating AA?

A7: Thanks for your suggestion. Some acid anhydrides were stable against water (Rong et al., 2020), and some others could be hydrolyzed to form organic acids in aqueous phase (Fritzler et al., 2014). The hydrolysis reactions of acid anhydrides were usually accelerated significantly by some catalysts (Faria et al., 2008). In the gas phase, α-acyloxyalkyl hydroperoxides formed from SCIs reaction with AA could dehydrate and form acid anhydrides (Long et al., 2009), and the reintroduction of water on anhydrides might not be easy to happen. The hydrolysis of acid anhydrides was expected to occur after anhydrides were taken up into atmospheric liquid water (Taatjes et al., 2019). Considering that the reaction time in this study was just a few minutes, this process was not predicted to be important.

Q8. Line 391-392 - “On the other hand” is repeated in the same sentence.

A8: Thanks for your suggestion. We have revised that in the manuscript.

Q9. Line 173 - k(other) - I wonder if wall loss of SCIs should be included in k(other)?

A9: Yes. Although the wall loss of SCIs was difficult to estimate and was not discussed in detail, we think the rate of wall loss of SCIs could be included in $k_{\text{(other)}}$.

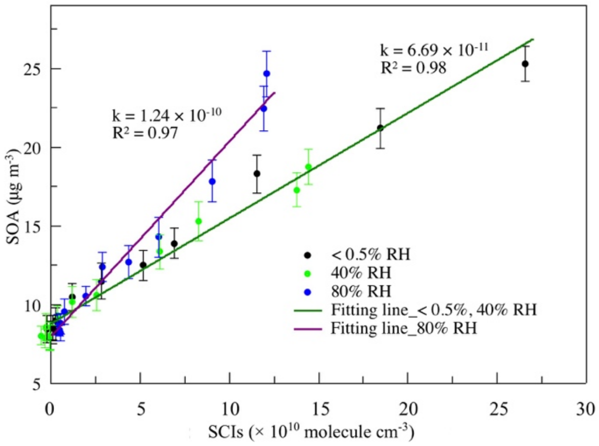


Figure S8. The dependence of SOA mass concentration on the amount of SCIs at different relative humidity (RH) in the first-generation oxidation with cyclohexane as OH scavenger.

Reference

Anglada, J. M., Aplincourt, P., Bofill, J. M., and Cremer, D.: Atmospheric formation of OH radicals and H_2O_2 from alkene ozonolysis under humid conditions, Chem. Phys. Chem., 3, 215–221, doi: 10.1002/1439-7641(20020215)3:2<215::Aid-Cphc215>3.3.Co;2-V, 2002.

Anglada, J. M., González, J., and Torrent-Sucarrat, M.: Effects of the substituents on the reactivity of carbonyl oxides. A theoretical study on the reaction of substituted carbonyl oxides with water, Phys. Chem. Chem. Phys., 13, 13034–13045, doi: 10.1039/C1CP20872A, 2011.

Aplincourt, P. and Anglada, J. M.: Theoretical studies of the isoprene ozonolysis under tropospheric conditions. 2. Unimolecular and water-assisted decomposition of the α-hydroxy hydroperoxides, J. Phys. Chem. A, 107, 5812–5820, doi: 10.1021/jp034203w, 2003.

Carslaw, N.: A new detailed chemical model for indoor air pollution, Atmos. Environ., 41, 1164–1179, doi: 10.1016/j.atmosenv.2006.09.038, 2007.

Chen, L., Wang, W. L., Wang, W. N., Liu, Y. L., Liu, F. Y., Liu, N., and Wang, B. Z.: Water-catalyzed decomposition of the simplest Criegee intermediate CH_2OO, Theor. Chem. Acc., 135, 131, doi: 10.1007/s00214-016-1894-9, 2016.

Chew, A. A. and Atkinson, R.: OH radical formation yields from the gas-phase reactions of O_3 with alkenes and monoterpenes, J. Geophys. Res., 101, 28649–28653, doi: 10.1029/96JD02722, 1996.

Crehuet, R., Anglada, J. M., and Bofill, J. M.: Tropospheric formation of hydroxymethyl hydroperoxide, formic acid, H_2O_2, and OH from carbonyl oxide in the presence of water vapor: A theoretical study of the reaction mechanism, Chem. Eur. J., 7, 2227–2235, doi: 10.1002/1521-3765(20010518)7:10<2227::AID-CHEM2227>3.0.CO;2-O, 2001.

Docherty, K. S. and Ziemann, P. J.: Effects of stabilized Criegee intermediate and OH radical scavengers on aerosol formation from reactions of β-pinene with O_3, Aerosol Sci. Technol., 37, 877–891, doi: 10.1080/02786820300930, 2003.

Faria, A. C., Mello, R. S., Orth, E. S., and Nome, F.: Hydrolysis of benzoic anhydride mediated by ionenes and micelles, J. Mol. Catal. A: Chem., 289, 106−111, doi: 10.1016/j.molcata.2008.04.019, 2008.

Fritzler, B. C., Dharmavaram, S., Hartrim, R. T., and Diffendall, G. F.: Acetic anhydride hydrolysis at high acetic anhydride to water ratios, Int. J. Chem. Kinet., 46, 151−160, doi: 10.1002/kin.20838, 2014.

Gong, Y. W., Chen, Z. M., and Li, H.: The oxidation regime and SOA composition in limonene ozonolysis: roles of different double bonds, radicals, and water, Atmos. Chem. Phys., 18, 15105–15123, doi: 10.5194/acp-18-15105-2018, 2018.

Jonsson, A. M., Hallquist, M., and Ljungström, E.: Influence of OH scavenger on the water effect on secondary organic aerosol formation from ozonolysis of limonene, 3-carene, and α-pinene, Environ. Sci. Technol., 42, 5938–5944, doi: 10.1021/es702508y, 2008.

Keywood, M. D., Kroll, J. H., Varutbangkul, V., Bahreini, R., Flagan, R. C., and Seinfeld, J. H.: Secondary organic aerosol formation from cyclohexene ozonolysis: Effect of OH scavenger and the role of radical chemistry, Environ. Sci. Technol., 38, 3343–3350, doi: 10.1021/es049725j, 2004.

Khan, M. A. H., Percival, C. J., Caravan, R. L., Taatjes, C. A., and Shallcross, D. E.: Criegee intermediates and their impacts on the troposphere, Environ. Sci.: Processes Impacts, 20, 437–453, doi: 10.1039/C7EM00585G, 2018.

Kumar, M., Busch, D. H., Subramaniam, B., and Thompson, W. H.: Role of tunable acid catalysis in decomposition of hydroxyalkyl hydroperoxides and mechanistic implications for tropospheric chemistry, J. Phys. Chem. A, 118, 9701–9711, doi: 10.1021/jp505100x, 2014.

Lin, J. J. M. and Chao, W.: Structure-dependent reactivity of Criegee intermediates studied with spectroscopic methods, Chem. Soc. Rev., 46, 7483–7497, doi: 10.1039/C7CS00336F, 2017.

Long, B., Cheng, J. R., Tan, X. F., and Zhang, W. J.: Theoretical study on the detailed reaction mechanisms of carbonyl oxide with formic acid, J. Mol. Struct.: THEOCHEM, 916, 159−167, doi: 10.1016/j.theochem.2009.09.028, 2009.

Rong, H., Liu, L., Liu, J. R., and Zhang, X. H.: Glyoxylic sulfuric anhydride from the gas-phase reaction between glyoxylic acid and SO_3: a potential nucleation precursor, J. Phys. Chem. A, 124, 3261−3268, doi: 10.1021/acs.jpca.0c01558, 2020.

Taatjes, C. A., Khan, M. A. H., Eskola, A. J., Percival, C. J., Osborn, D. L., Wallington, T. J., and Shallcross, D. E.: Reaction of perfluorooctanoic acid with Criegee intermediates and implications for the atmospheric fate of perfluorocarboxylic acids, Environ. Sci. Technol., 53, 1245−1251, doi: 10.1021/acs.est.8b05073, 2019.

Vereecken, L., Harder, H., and Novelli, A.: The reaction of Criegee intermediates with NO, RO_2, and SO_2, and their fate in the atmosphere, Phys. Chem. Chem. Phys., 14, 14682–14695, doi: 10.1039/c2cp42300f, 2012.

Wang, Y., Kim, H., and Paulson, S. E.: Hydrogen peroxide generation from α- and β-pinene and toluene secondary organic aerosols, Atmos. Environ., 45, 3149–3156, doi: 10.1016/j.atmosenv.2011.02.060, 2011.

Winterhalter, R., Neeb, P., Grossmann, D., Kolloff, A., Horie, O., and Moortgat, G.: Products and mechanism of the gas phase reaction of ozone with β-pinene, J. Atmos. Chem, 35, 165–197, doi: 10.1023/A:1006257800929, 2000.

Zhao, Q. L., Liu, F. Y., Wang, W. N., Li, C. Y., L*ü*, J., and Wang, W. L.: Reactions between hydroxyl-substituted alkylperoxy radicals and Criegee intermediates: correlations of the electronic characteristics of methyl substituents and the reactivity, Chem. Chem. Phys., 19, 15073, doi: 10.1039/c7cp00869d, 2017.

Zhao, R., Kenseth, C. M., Huang, Y. L., Dalleska, N. F., Kuang, X. M., Chen, J. R., Paulson, S. E., and Seinfeld, J. H.: Rapid aqueous-phase hydrolysis of ester hydroperoxides arising from Criegee intermediates and organic acids, J. Phys. Chem. A, 122, 5190−5201, doi: 10.1021/acs.jpca.8b02195, 2018.

Quantification of the role of stabilized Criegee intermediates in the formation of aerosols in limonene ozonolysis

Yiwei Gong[1] and Zhongming Chen[1]

[1]State Key Laboratory of Environmental Simulation and Pollution Control, College of Environmental Sciences and Engineering, Peking University, Beijing 100871, China

Correspondence to: Z. M. Chen (zmchen@pku.edu.cn)

Abstract. Stabilized Criegee intermediates (SCIs) have the potential to oxidize trace species and to produce secondary organic aerosols (SOA), making them important factors in tropospheric chemistry. This study quantitatively investigates the performance of SCIs in SOA formation at different relative humidity (RH), and the first- and second-generation oxidations of endo- and exo-cyclic double bonds ozonated in limonene ozonolysis are studied separately. Through regulating SCIs scavengers, the yields and rate constants of SCIs in reaction system were derived, and the amounts of SCIs were calculated. The amount of SOA decreased by more than 20% under low-humidity conditions (10–50% RH), compared to that under dry conditions due to the reactions of SCIs with water, while the inhibitory effect of water on SOA formation was not observed under high-humidity conditions (60–90% RH). When using excessive SCIs scavengers to exclude SCIs reactions, it was found that the effect of water on SOA formation with the presence of SCIs was different from that without the presence of SCIs, suggesting that SCIs reactions were relevant to the non-monotonic impact of water. The fractions of SCIs contribution to SOA were similar between dry and high-humidity conditions, where the SCIs reactions accounted for ~ 63% and ~ 73% in SOA formation in the first- and second-generation oxidation, however, marked differences in SOA formation mechanisms were observed. SOA formation showed a positive correlation with the amount of SCIs, and the SOA formation potential of SCIs under high-humidity conditions was more significant than that under dry and low-humidity conditions. It was estimated that 20–30% of SCIs could convert into SOA under high-humidity conditions, while this value decreased nearly by half under dry and low-humidity conditions. The typical contribution of limonene-derived SCIs to SOA formation is calculated to be $(8.21 \pm 0.15) \times 10^{-2}$ μg m^{-3} h^{-1} in forest, $(4.26 \pm 0.46) \times 10^{-2}$ μg m^{-3} h^{-1} in urban area, and $(2.52 \pm 0.28) \times 10^{-1}$ μg m^{-3} h^{-1} in indoor area. ~~The contributions of limonene-derived SCIs to SOA in the atmosphere were evaluated, and it was estimated that the contribution of SCIs to SOA was the lowest under low-humidity conditions. Under high-humidity conditions, the contribution of limonene-derived SCIs to SOA was $(8.21 \pm 0.15) \times 10^{-2}$ μg m^{-3} h^{-1} in forest, $(6.66 \pm 0.12) \times 10^{-2}$ μg m^{-3} h^{-1} in urban area, and $(3.95 \pm 0.72) \times 10^{-1}$ μg m^{-3} h^{-1} in indoor area.~~ Water is~~was~~ an uncertainty on the role of SCIs playing in SOA formation, and the contribution of SCIs to SOA formation needs~~needed~~ consideration even under high RH in the atmosphere.

1 Introduction

Stabilized Criegee intermediates (SCIs), formed from the stabilization of excited Criegee intermediates (ECIs) during the ozonolysis of alkenes, play important roles in atmospheric chemistry (Criegee and Wenner, 1949; Drozd and Donahue, 2011; Johnson and Marston, 2008; Khan et al., 2017; Ziemann and Atkinson, 2012). Although these reactive species have been known for decades, it is only recently that the synthesis and measurement of some simple SCIs has become possible (Sheps et al., 2014; Taatjes et al., 2008, 2013; Welz et al., 2012). SCIs can oxidize a series of trace species in the atmosphere, such as SO_2, NO_x, carboxylic acids, carbonyl compounds, alcohols, etc. (Berndt et al., 2015; Elsamra et al., 2016; Khan et al., 2018; Mauldin III et al., 2012; Taatjes et al., 2014), and the reaction rate constants reported in the last few years are several orders of magnitude larger than the values estimated earlier (Osborn and Taatjes, 2015; Sander, 2014; Taatjes, 2017), indicating that the contribution of SCIs to atmospheric oxidizing capacity should not be neglected. Reactions of SCIs are also important in secondary organic aerosol (SOA) formation because some bimolecular reactions of SCIs produce low-volatile products (Chhantyal-Pun et al., 2018; Kim et al., 2015; McGillen et al., 2017). In addition, SCIs are reported to participate in chain reactions with RO_2 radicals and carboxylic acids resulting in oligomers formation (Sakamoto et al., 2013; Zhao et al., 2015). The reaction pathways of SCIs in ozonolysis systems are complex, and it is difficult to determine the reaction mechanism of each pathway, especially for those complex SCIs such as monoterpene-derived SCIs. Although the important role of SCIs in aerosol formation has been claimed, a quantitative study of the contribution of SCIs to SOA in alkenes ozonolysis is lacking. Among the SCIs generated, the amount of SCIs that would participate in aerosols formation and the effects of experimental conditions remain unknown. These questions have not been investigated in detail, yet they are important for promoting our understanding of the fate of SCIs in alkenes ozonolysis.

In the past years, many efforts have been devoted to studying the reaction mechanisms of SCIs. Some matters remain in dispute and one of them is the effect of water. Through synthesizing and measuring SCIs containing less than three carbon atoms, it is found that the reaction of SCIs and water is structure-dependent, while the reaction mechanisms of more complex SCIs are still unclear because of the lack of synthesis and direct measurements (Huang et al., 2015; Lin and Chao, 2017). In addition to acting as a gas-phase sink of SCIs, water promotes the heterogeneous reactions of SCIs on aqueous surfaces (Enami and Colussi, 2017a; Kumar et al., 2018), which are purported to occur on the surfaces of droplets, aerosols, seas, etc. SCIs reactions at air-water interfaces have drawn much attention in recent years because of the high reactivity of SCIs on aqueous surfaces, especially as applies to the large surface areas present in the atmosphere (Zhong et al., 2018). In the ozonolysis of alkenes, the presence of water changes the reaction pathways of SCIs, while the yields of products, such as peroxides and carbonyls, formed from SCIs reactions with water have been reported to vary widely (Berndt et al., 2003; Huang et al., 2013; Li et al., 2016~~; Berndt et al., 2003~~). Furthermore, the dependences of these products on relative humidity (RH) have been a point of controversy (Anglada et al, 2002; Hasson et al., 2001, 2003; Ma et al., 2008; Tillmann et al., 2010). In ozonolysis system examining the effects of the addition of compounds that could be oxidized by SCIs, the presence of water had different effects on the consumption of these added reactants (Newland et al., 2018; Sipilä et al., 2014; Ye et al., 2018). The reactions of SCIs with water further impact the generation of semi-volatile organic compounds (SVOCs) and low-volatile organic compounds (LVOCs), resulting in changes of SOA yield and composition. It is intriguing to note that previous studies presented positive, negative, and neutral effects of water on aerosol formation in alkenes ozonolysis (Bonn et al., 2002; Bracco et al., 2019; Hessberg et al., 2009; Jonsson et al., 2008; Li et al., 2019; Warren et al., 2009; Yu et al., 2011), indicating that the uncertainty and complexity of SOA formation as RH changes need further research.

Previous studies have mainly chosen smog chambers as reaction equipment, yet the long reaction time and the large wall loss may significantly affect the analysis results (Chuang and Donahue, 2017; Zhang et al., 2014, 2015). As reported by Brune et al. (2019), the Chamber Wall Index, which could be used to evaluate the degree that walls alter the chemistry, demonstrates that the wall effect in flow reactors is smaller than that in chambers. In this study, experiments were carried out in flow tube reactors to constrain the reaction time within a few minutes, with the hope of reducing the wall loss effect and allowing observation of the products generated in the initial state of the reaction. Limonene is selected as the model compound for this research, not only because of the large emissions of limonene both from biogenic and anthropogenic sources (Andersson-Sköld and Simpson, 2001; Atkinson and Arey, 2003), but also because of the high SOA formation potential of limonene as a double-unsaturated terpene (Lee et al., 2006; Ng et al., 2006). This study focuses on quantifying the impact of SCIs on aerosol formation at different RH, and SCIs scavengers are used to control the amounts of SCIs in the reaction system. In order to have a complete understanding of limonene-derived SCIs, our research strategy consisted of two sets of experiments, which separately investigated the first-generation oxidation with endocyclic double bonds (endo-DB) ozonated and the second-generation oxidation with exocyclic double bonds (exo-DB) ozonated.

2 Experimental

2.1 Apparatus and procedures

One-stage and two-stage apparatuses were used to investigate SOA formation in the first- and second-generation oxidations, respectively. Limonene ozonolysis primarily took place on endo-DB, with a rate constant of 2×10^{-16} cm^3 molecule^{-1} s^{-1} (Atkinson, 1990; Shu and Atkinson, 1994), and the exo-DB reaction with O_3 was about 30 times slower (Pathak et al., 2012). In the first set of experiments focusing on the first-generation oxidation, we used an 8 L quartz flow tube reactor (2 m length, 70 mm inner diameter), which was equipped with a water jacket to control the reaction temperature at 298.0 ± 0.5 K. Gas containing limonene was generated with a diffusion tube kept at a specific temperature, and the concentration of limonene was detected to be 90.0 ± 1.5 ppbv by a gas chromatograph with a flame ionization detector (GC-Agilent 7890A, USA). O_3 was generated through photolysis of pure oxygen with a low-pressure Hg lamp, and the concentration of O_3 was detected to be 270.0 ± 3.0 ppbv by indigo disulphonate spectrophotometry. To avoid the disturbance by OH radicals, excessive 2-butanol was generated with a bubbler and added to the reactor as an OH scavenger. The concentration of 2-butanol was 300.0 ± 6.0 ppmv and was estimated to be sufficient for scavenging more than 99% OH radicals. Acetic acid (AA), which has been considered as an efficient SCIs scavenger due to the rapid reaction of SCIs with AA (Ahmad et al., 2017; Yao et al., 2014), was used as an SCIs scavenger in this study. Gas containing AA was prepared by an evacuated steel canister (15 L, Entech Instruments), of which the outlet was linked with a mass flow controller to regulate the gas flow rate. Water vapor was produced by passing N_2 or O_2 through a water bubbler, and the RH in reactor ranged from dry condition (< 0.5% RH) to 90 ± 3% RH. Chemicals used in this study were shown in the Supplement. Gases containing limonene, O_3, 2-butanol, AA, and water vapor were rapidly blended in a mixing ball and successively introduced into the flow tube reactor. The total gas flow rate was 2 standard L min^{-1} and the residence time was 240 s. In the first set of experiments, endo-DB consumed by O_3 was estimated to be ~ 24.6 ppbv, while exo-DB ozonolysis was not taken into account.

In the second set of experiments focusing on the second-generation oxidation, we used a two-stage apparatus including a 2 L quartz flow tube reactor (1 m length, 50 mm inner diameter) and an 8 L quartz flow tube reactor (2 m length, 70 mm inner diameter) in series. The experiments were performed at 298.0 ± 0.5 K in the dark, and the diagram of the reaction equipment is shown in Fig. 1. To investigate the exo-DB oxidation alone a key point was separating the endo-DB reaction, so the major role of the first stage was to accomplish the reaction of endo-DB with O_3. Although it was unavoidable that some exo-DB also reacted with O_3 in the first stage, this would not impact the analysis of the second-generation oxidation in the second stage because the quantitative investigation only focused on the exo-DB ozonated in the second-stage. The initial concentrations of limonene and O_3 in the first stage were 46.2 ± 1.0 ppbv and 12.2 ± 0.3 ppmv, respectively, and excessive 2-butanol was added to scavenge OH radicals. With a total flow rate of 1.95 standard L min^{-1}, the residence time in the first stage was 65 s and the remaining limonene was estimated to be less than 0.4 ppbv. Before entering the second reactor, gas containing different concentrations of AA was added to mix with the gas out of the first reactor. The total flow rate in the second stage was 2 standard L min^{-1}, and it was estimated that the amount of exo-DB that was ozonated was ~ 15.2 ppbv. Assuming a typical 24 h average ambient O_3 concentration of 30.0 ppbv (Palm et al., 2018), the equivalent atmospheric times of O_3 exposure in the first- and second-generation oxidations were 0.6 h and 26.4 h, respectively.

2.2 Measurements

To detect the concentration of AA, gas samples out of the reactor were collected in a glass coil collector rinsed by ultrapure water (18 MΩ) at 277 K. The effective length of the coil collector was ~ 100 cm, in which the flow rates of gas and water were 0.9 standard L min^{-1} and 0.2 mL min^{-1}, respectively. The coil collector, shown as a diagram in the Supplement, was as elaborated before (Hua et al., 2008), and the percentage of AA dissolved in the rinsing solution was calculated to be higher than 99% based on Henry's law when the partitioning between gas phase and liquid phase was at equilibrium (Lazrus et al., 1986). Samples of extracting solution were analyzed by an ion chromatography (IC, DIONEX ICS-2000) with the detection limit of ~ 50 pptv, and the standard solution of AA was prepared to perform calibrations in every measurement. Wall loss experiments were carried out by introducing gas containing AA to the reactor at 2 standard L min^{-1}, and the inlet and outlet concentrations of AA at different RH were measured. The loss fraction of AA in the 8 L flow tube was found to be less than 8% without distinct influence by RH, and the results reported below were rectified by the wall loss effect. In both of the first- and second-generation oxidations, when no AA was added, the background level of AA was detected to be less than 1.0 ppbv, which was subtracted from the results.

Particle size distribution was measured by a scanning Mobility Particle Sizer (SMPS, 3938, TSI) consisting of a differential mobility analyzer (DMA, 3081A) and a condensation particle counter (CPC, 3776). The measurement was in the range of 13.8–504.8 nm, and the interval was 5 min. The sampling flow rate of SMPS was 0.3 L min^{-1} and the sheath air flow was 3 L min^{-1}. All data were treated with multiple charge correction and diffusion loss correction by the TSI software, and the aerosol density was assumed to be 1.3 g cm^{-3} when calculating the aerosol mass concentration (Saathoff et al., 2009; Wilson et al., 2015). The gas flow in the 8 L flow reactor was evaluated to be laminar as the Reynolds number was ~ 43 (Ezell et al., 2010), and to better observe the process of SOA formation during the reaction, a stainless tube, which was flexible in the axial direction, was used to collect samples at different positions in the reactor. As the gas sample extracted from the stainless steel tube was a small part of the total gas flow, the whole flow state in the reactor could remain stable. The gas samples collected at different positions represented products formed under different reaction times. The measurement of the SOA formation process in the 8 L flow reactor started after the reaction had proceeded for 60 s, and the sampling interval was set as 30 s. It was noted that this method was used to assist us to know the processes of SOA formation in the first- and second-generation oxidation. The calculations and analysis in this study used the samples collected at the end of the reactor. The aerosol wall loss experiments were performed as our previous study (Gong et al., 2018), and the loss fraction of SOA mass concentration was found to increase when RH increased as shown in Table S1. The mass concentration of SOA was also subtracted by the water content according to the hygroscopic growth factor reported before (Bateman et al., 2015).

3 Results and discussion

3.1 Regulating and quantifying the amount of SCIs

To quantitatively investigate the performance of SCIs in SOA formation, the amount of SCIs in the reaction system was regulated by adding different concentrations of AA (24–480 ppbv) at a series of RH (< 0.5%, 10%, 40%, 60%, 80%). Both of AA and water could react with SCIs, and here the amount of SCIs in reaction system is defined as the accumulated amount of SCIs that are not consumed by AA and water, and it could be derived by deducting the amount of SCIs reacted with AA and water from the amount of total SCIs generated. Limonene ozonolysis generates several kinds of SCIs (Leungsakul et al., 2005), which are difficult to distinguish. As reported before, SCIs reaction with water is structure-dependent, and here all SCIs are divided into two types, one of which tends to react with water (SCI$_{\mathrm{I}}$), and the other is inert to react with water (SCI$_{\mathrm{II}}$) (Long et al., 2018). The molar yield of SCIs, defined as the ratio of SCIs mole number to the mole number of DB ozonated, could be inferred through measuring the consumption of AA (ΔAA). This calculation was based on two points: first, previous studies reported that SCIs reaction with AA was rapid and not structure-dependent (Khan et al., 2018); second, as we described below, the SCIs yield derived from reaction with AA was higher than that derived from reaction with water, confirming that both kinds of limonene-derived SCIs reacted effectively with AA. With the increase of AA concentration, ΔAA increased in the beginning and then became stable. According to the maximum ΔAA under dry conditions, the SCIs yield of endo-DB ozonated was calculated to be ~ 0.44. Through measuring the generation of H_2O_2 (in the Supplement), the yield of SCI_I in endo-DB ozonated was reported to be ~ 0.24 (Gong et al., 2018), and thus the yield of SCI_{II} was derived to be ~ 0.20.

For the amount of SCIs consumed by SCIs scavengers, ΔAA represented the amount of SCIs consumed by AA, and the amount of SCIs consumed by water was calculated through the reaction rate ratio of SCIs reaction with water and AA, which was elaborated in the Supplement. The ratio of rate constants of SCIs reaction with water and AA was derived from the estimation of ΔAA as shown in Fig. 2. Due to the competition with water, the variation of ΔAA under high-humidity conditions was gentler than that under dry conditions. The relationship between ΔAA and the concentration of AA is estimated according to Eqs. (1) to (3) (Bracco et al., 2019; Hessberg et al., 2009):

$$\frac{SCI_{AA}}{SCI_{Total}} = \frac{\Delta AA}{SCI_{Total}} = \frac{k_{(SCI+AA)} \cdot [AA]}{k_{(SCI+AA)} \cdot [AA] + k_{(SCI+H2O)} \cdot [H_2O] + k_{(other)}} \tag{1}$$

$$\Delta AA = \frac{1}{1 + \frac{k_{(SCI+H2O)} \cdot [H_2O] + k_{(other)}}{k_{(SCI+AA)} \cdot [AA]}} \cdot SCI_{Total} \tag{2}$$

$$\Delta AA = \frac{SCI_{\mathrm{I}}}{1 + \frac{k_{(SCI+H2O)\mathrm{I}} \cdot [H_2O] + k_{(other)\mathrm{I}}}{k_{(SCI+AA)} \cdot [AA]}} + \frac{SCI_{\mathrm{II}}}{1 + \frac{k_{(other)\mathrm{II}}}{k_{(SCI+AA)} \cdot [AA]}} \tag{3}$$

where SCI_{AA} (molecule cm^{-3}) is the amount of SCIs reacted with AA; SCI_{Total} (molecule cm^{-3}) is the amount of total SCIs generated; ΔAA (molecule cm^{-3}) is the amount of AA consumed; $k_{(SCI+AA)}$ (cm^3 $molecule^{-1}$ s^{-1}) is the rate constant of SCIs reaction with AA; [AA] (molecule cm^{-3}) is the concentration of AA; $k_{(SCI+H2O)}$ (cm^3 $molecule^{-1}$ s^{-1}) is the rate constant of SCIs reaction with H_2O; [H_2O] (molecule cm^{-3}) is the concentration of H_2O; $k_{(other)} = k_{(isomerization)} + k_{(SCI+products)} \cdot [products]$, meaning that $k_{(other)}$ accounts for the sum of SCIs isomerization and reaction with other products in the system. Equation (2) could be extended to Eq. (3) containing two types of SCIs. One consideration in calculations is whether the reaction with H_2O or with $(H_2O)_2$ dominates in SCI_I reaction with water, which is discussed in the Supplement. Results showed that the reaction with H_2O was more important in this reaction system, and the values of $k_{(SCI+H2O)I}$ and $k_{(other)I}$ were derived to be 5×10^{-16} cm^3 $molecule^{-1}$ s^{-1} and 30 s^{-1} (Fig. S2). Estimations of ΔAA at < 0.5% and 80% RH were calculated and shown in Fig. 2, where $k_{(SCI+AA)}$ and $k_{(other)II}$ were derived to be 1×10^{-10} cm^3 $molecule^{-1}$ s^{-1} and 100 s^{-1}, respectively. The ratio of rate constants of SCIs reaction with water and AA was 5×10^{-6} and the amounts of SCIs under different conditions were shown in Table S2.

In the second-generation oxidation, according to the maximum ΔAA under dry conditions, the SCIs yield of exo-DB ozonated was calculated to be ~ 0.60. As RH increased to 40%, ΔAA became smaller than that under dry conditions because of the competition of water. However, at 60% RH, ΔAA performed a rise and at 80% RH the maximum of ΔAA increased to be about double of that under dry conditions, suggesting that more SCIs were generated due to more exo-DB ozonated. The amount of exo-DB ozonated under high-humidity conditions could be derived through estimating the variation of ΔAA.

Through calculating the formation of H_2O_2 as described above, the yields of SCI_I and SCI_{II} in the second-generation oxidation were both assumed to be 0.30. According to the calculation results (Fig. S3), the amounts of exo-DB ozonated at 60% and 80% RH were 1.3 and 2.0 times of that under dry conditions. If particles were treated as liquid state under high-humidity conditions, the amount of exo-DB reaction with O_3 in aerosols was calculated in the Supplement. Bulk-phase ozonolysis could not explain the exo-DB ozonated, suggesting that reactions on surfaces were more important. Some studies reported the uptake and ozonation of terpenes on aqueous surfaces (Enami et al., 2010; Matsuoka et al., 2017), and as for those semi-volatile products containing exo-DB, their uptake on aqueous surfaces might have a greater chance to happen due to the lower volatility. This study reported direct evidence for the heterogeneous oxidation of exo-DB of limonene, which was proposed before by Zhang et al. (2006). The uptake coefficient of these unsaturated products was estimated to be 10^{-3} of magnitude, which was elaborated in the Supplement. The amounts of SCIs in the second stage under different conditions were calculated and appeared in Table S3.

3.2 The effect of water on SOA formation

3.2.1 Water effect with the presence of SCIs

In ozonolysis water could participate in some reactions and it is necessary to investigate SOA formation under different RH. When investigating the SOA formation process experiments were carried out from < 0.5% RH to 90% RH with the interval of 10% RH. Through calculating the amounts of limonene reacted at different reaction times, the growth curves of SOA mass concentration and SOA yield could be derived in the first-generation oxidation, as shown in Fig. S4. SOA yield was determined from the mass concentration of SOA divided by the mass concentration of limonene reacted. As RH increased, SOA formation presented non-monotonic dependence on RH. The presence of water suppressed the process of SOA formation under low-humidity conditions (10–50% RH), while the inhibitory effect of water on SOA formation was not observed under high-humidity conditions (60–90% RH). The SOA yields at the end of the first-generation oxidation under dry and high-humidity conditions were ~ 20%, and under low-humidity conditions the SOA yield was ~ 15%. In the second-generation oxidation, SOA growth was observed due to exo-DB ozonolysis, and the increase of SOA mass concentration (ΔSOA) was derived by subtracting the SOA mass concentration at the end of the first stage from that at the end of the second stage. Because limonene was almost consumed in the first stage, the variations of SOA mass concentration and SOA yield in the second stage are shown as a function of reaction time (Fig. S5). The inhibitory effect of water on SOA formation under low-humidity conditions was also observed with a ΔSOA reduction of as much as ~ 22%. Under high-humidity conditions, SOA growth became more intense due to more exo-DB ozonated, and the increment of SOA yield above 80% RH was more than twice that under dry conditions.

3.2.2 Water effect without the presence of SCIs

To figure out the fraction of SCIs reactions contributing to SOA formation, excess AA (10.0 ± 0.4 ppmv) was added to scavenge all SCIs in the reaction system. The concentration of AA used here was estimated to be sufficient for scavenging more than 99% of SCIs generated during reactions as claimed in the Supplement. Without the presence of SCIs, the amount of SOA decreased dramatically both in the first- and second-generation oxidation, indicating that the reaction with AA converted SCIs into more volatile products. The mechanisms of SCIs reaction with carboxylic acids were not entirely clear, and two reaction pathways were proposed. The insertion products, produced from hydroperoxyester channel, would go through water elimination and formed acid anhydride (Aplincourt and Ruiz-López, 2000; Cabezas and Endo, 2020; Long et al., 2009). As the molecular weight of AA was small, the contribution of acid anhydride produced to SOA might be limited. Some studies suggested that SCIs reaction with acids proceeded via acid-catalyzed tautomerization of SCIs to vinyl hydroperoxides, which were not likely to contribute to aerosols (Kumar et al., 2014a; Liu et al., 2015). Besides, it was observed that when scavenging the same amount of SCIs by AA and water the decreases of SOA were similar. Thus, it was estimated that the contribution of the products formed from SCIs reaction with AA to aerosols was small. Through excluding the impact of SCIs, it was found that SCIs reactions accounted for ~ 63% and ~ 73% of the total SOA formed under dry conditions in the first- and second-generation oxidation.

Figure 3 shows how the presence of SCIs impacts SOA formation, and the influence of water on SOA formation with the presence of SCIs was different from that without the presence of SCIs. The inhibitory effect of water on SOA formation could be attributed to the reaction between SCIs and water, producing α-hydroxyalkyl hydroperoxides, which were thought to preferentially decompose to H_2O_2 and aldehydes (Chen et al., 2016; Jiang et al., 2013; Kumar et al., 2014b; Winterhalter et al., 2000). The aldehydes, such as pinonaldehyde and nopinone formed from α-pinene-derived and β-pinene-derived SCIs reaction with water, displayed higher volatility and their contribution to aerosols was reported to be small in ozonolysis (Emanuelsson et al., 2013; Fick et al., 2003; Jenkin, 2004; Mutzel et al., 2016; Sakamoto et al., 2017). An intriguing finding here was that the amount of SOA formed under high-humidity conditions increased, and one possible reason for this phenomenon was the physical effect of water, as the viscosity of particles would decrease due to the uptake of water resulting in the transition of particles from non-liquid to liquid state with increasing RH (Faust et al., 2017; Renbaum-Wolff et al., 2013). The low viscosity of particles further improved the particle-phase diffusion and gas-particle partitioning of SVOCs (Shiraiwa and Seinfeld, 2012; Ye et al., 2016). Nevertheless, some studies reported that the SOA formation process in monoterpene ozonolysis was quasi-equilibrium growth, meaning that the timescales of gas-particle partitioning equilibrium and diffusion in particles were much smaller than the timescales of gas-phase reactions and the wall loss process (McVay et al., 2014, 2016; Nah et al., 2016, 2017; Riipinen et al., 2011). Results showed that when SCIs were scavenged in the first-generation oxidation, the amount of SOA was almost unaffected by RH. Besides, considering that the diameters of most particles generated in the experiments were smaller than 100 nm, and the effect of water on the diffusion limit was not considered as the major cause of the increase of SOA under high-humidity conditions (Tu and Johnson, 2017; Veghte et al., 2013). Figure 4 shows the dependence of the fraction of SCIs contribution to SOA on RH, and it was found that in both of the first- and second-generation oxidations the contribution of SCIs reactions to SOA formation decreased under low-humidity conditions and increased under high-humidity conditions, suggesting that the non-monotonic effect of water on SOA formation was relevant to SCIs reactions.

3.3 The correlation between SCIs and SOA formation

3.3.1 Quantifying the fraction of SCIs converting into SOA

The variation of SOA with the concentration of AA at different RH in the first-generation oxidation was shown in Fig. 5. Although the amount of SOA formed under dry and high-humidity conditions were similar, their variations were different with increasing AA, indicating that differences existed in SOA formation mechanisms between dry and high-humidity conditions. To figure out the correlation between SCIs and SOA formation, the dependence of SOA mass concentration on the amount of SCIs is shown in Fig. 6, where the dependences under dry and low-humidity conditions are similar to each other with the deviation among their slopes of linear fitting lines falling within 15%. The fitting lines under high-humidity conditions are also similar. The fact that the correlation coefficients (R^2 values) of the fitting lines are greater than 0.9 indicates that the amount of SOA generated has a significant positive correlation with the amount of SCIs, regardless of RH and oxidation degree. In the first-generation oxidation, the slope of the fitting line under dry and low-humidity conditions is 6.26×10^{-11}, and the slope under high-humidity conditions is 1.05×10^{-10}. In the second-generation oxidation, the slope of the fitting line under dry and low-humidity conditions is 5.08×10^{-11}, and the slope of the fitting line at 60% RH is 9.43×10^{-11}, which is similar to the value of 1.08×10^{-10} at 80% RH. The slopes of fitting lines in the first- and second-generation oxidations under dry and low-humidity conditions were similar, as were the fitting results under high-humidity conditions, suggesting that the role of SCIs in SOA formation was slightly affected by the oxidation degree in limonene ozonolysis. Based on the correlation between SOA formation and SCIs, the SOA yield of limonene-derived SCIs could be inferred from the mass concentration of SOA formed from SCIs reactions divided by the mass concentration of SCIs reacted. The SOA yield of limonene-derived SCIs was estimated to be ~ 0.20 under dry and low-humidity conditions and ~ 0.35 under high-humidity conditions. From another view, results showed that among the SCIs in reaction system, the fraction that could produce low-volatile products and convert into SOA was stable, and here the fraction was denoted as α_{SCI}. In this study α_{SCI} of limonene-derived SCIs was estimated to be 11–17% under dry and low-humidity conditions and 20–30% under high-humidity conditions, which was elaborated in the Supplement. Considering that part of products in particles were semi-volatile, α_{SCI} derived here was expected to be a lower limit, and this value was used to estimate the amount of SOA formed from SCIs reactions.

3.3.2 Analysis on reaction mechanisms

The SOA formation potential of SCIs under high-humidity conditions was found to be more significant than that under dry and low-humidity conditions, which needed explanations on reaction mechanisms. In ozonolysis the cycloaddition of O_3 to alkenes produced a primary ozonide (POZ), which decomposed to ECIs and aldehyde or ketone. ECIs can isomerize through hydroperoxide channel, rearrange to esters, or stabilize to form SCIs (Johnson and Marston, 2008). In this study, SOA formation was roughly divided into two pathways: directly from ECIs reactions and from SCIs reactions. According to the results, SOA formation directly from ECIs reactions was unaffected by changing RH. As for SCIs, the main reaction pathways concluded bimolecular reactions with products formed during ozonolysis (Lee and Kamens, 2005; Yao et al., 2014), unimolecular reactions producing vinyl-hydroperoxides, secondary ozonides, and dioxiranes, etc. (Long et al., 2019), and chain reactions producing oligomers (Sakamoto et al., 2013). The reaction scheme of limonene ozonolysis and the structures of proposed products were shown as Fig. 7. When discussing the behaviors of SCIs in SOA formation, side reactions of SCIs needed consideration and were analyzed below.

Since the concentration of O_3 in experiments was higher than the concentration of limonene, the reaction of SCIs with O_3 might impact products formation. A lower limit for the rate constant of SCIs reaction with O_3 of 10^{-18} cm^3 $molecule^{-1}$ s^{-1} was proposed at 298 K (Kjaergaard et al., 2013), and some studies derived a higher value of about 10^{-14} cm^3 $molecule^{-1}$ s^{-1} (Chang et al., 2018; Vereecken et al., 2015). The reaction of limonene-derived SCIs and O_3 was rarely reported, and we took the rate constant of 10^{-14} cm^3 $molecule^{-1}$ s^{-1} to estimate an upper limit for the amount of SCIs reacted with O_3. Taking SCIs reaction with AA as a reference, when using the lowest concentration of AA in experiments, the ratios of the amount of SCIs reacted with O_3 to the amount of SCIs reacted with AA were 0.001 and 0.046 in the first- and second-generation oxidation, respectively, indicating that the reaction of SCIs with O_3 was not important. SCIs could react with alcohols, and here the effect of this reaction was considered because in this study high concentration of 2-butanol was used to scavenge OH radicals. ~~The rate constants of CH_2OO reaction with methanol and ethanol were measured to be about 10^{-15} cm^3 $molecule^{-1}$ s^{-1} at 298 K (McGillen et al., 2017). Theoretical computation showed that the rate constants of CH_2OO and $(CH_3)_2COO$ reaction with methanol at 298 K were about 10^{-13} cm^3 $molecule^{-1}$ s^{-1} and 10^{-15} cm^3 $molecule^{-1}$ s^{-1}, respectively (Aroeira et al., 2019). When the rate constant of limonene-derived SCIs reaction with 2-butanol was assumed as 10^{-15} cm^3 $molecule^{-1}$ s^{-1}, it was estimated that with the lowest concentration of AA used in experiments, the ratio of the amount of SCIs reacted with 2-butanol to the amount of SCIs reacted with AA was 0.125, which was considered to be not important enough to influence the results.~~ Previous studies reported that as for the reactions of SCIs with alcohols, the substitution group of alcohols had little effect on the reactions, while the structures of SCIs showed an obvious influence. The rate constants of CH_2OO reaction with alcohols were about 10^{-13} cm^3 $molecule^{-1}$ s^{-1} at 298 K (Tadayon et al., 2018), and it was slower for $(CH_3)_2COO$ reaction with alcohols, whose rate constants were reported to be $10^{-15} \sim 10^{-14}$ cm^3 $molecule^{-1}$ s^{-1} (Aroeira et al., 2019; McGillen et al., 2017). Watson et al. (2019) computed that the rate constant of *syn*-CH_3CHOO + CH_3OH was about 10^{-17} cm^3 $molecule^{-1}$ s^{-1}, which was much smaller than that of about 10^{-12} cm^3 $molecule^{-1}$ s^{-1} for *anti*-CH_3CHOO + CH_3OH at 298 K. In limonene ozonolysis, several kinds of SCIs were produced and their structures were shown in Fig. S7. A mono-substituted SCIs and a di-substituted SCIs were formed from endo-DB ozonolysis, and exo-DB ozonolysis produced CH_2OO and a di-substituted SCIs. When assuming the rate constant of SCIs reaction with 2-butanol as 10^{-14} cm^3 $molecule^{-1}$ s^{-1}, it was estimated that in terms of the concentrations of AA used in experiments, the ratio of the amount of SCIs reacted with 2-butanol to the amount of SCIs reacted with AA ranged from 0.06 to 1.25, and this ratio might be higher in exo-DB oxidation because of the formation of CH_2OO. This meant that part of SCIs could react with 2-butanol, producing α-alkoxyalkyl-hydroperoxides and contributing to the observed SOA, especially when using low concentrations of AA and water. To figure out whether the SOA formation potentials of SCIs estimated here were higher than those under the situation without 2-butanol, the experiments with cyclohexane as OH scavenger were carried out, and the details were described in the Supplement. It was found that with the use of cyclohexane, SCIs reactions still accounted for more than 60% in SOA formation and according to the fitting results, the SOA formation potentials of SCIs were even a bit larger than those with the use of 2-butanol, and their deviations were within 12%. This phenomenon was speculated to be due to the higher concentration of RO_2 radicals when using cyclohexane, promoting the reactions of SCIs with RO_2. To further determine the impact of 2-butanol, we also conducted experiments with the concentration of 2-butanol as about 150 ppmv, which was half of the previous concentration of 2-butanol used in experiments and was estimated to be sufficient for scavenging more than 99% OH radicals. It was observed that the amount of SOA formation was not impacted by the concentration of 2-butanol, and the SOA formation potentials of SCIs under a lower concentration of 2-butanol were similar with those under a higher concentration of 2-butanol. Based on the results elaborated above, we confirmed that the effect of 2-butanol on the results was limited. Besides, products formed from SCIs reaction with AA and water might further react with SCIs and impacted aerosols formation (Chen et al., 2019). However, due to the short lifetime and low concentration of SCIs in system, the concentration of SCIs was a limiting factor in bimolecular reactions of SCIs with other products. ~~The reactions of SCIs with the compounds formed from SCIs scavengers would not compensate the effect of the consumption of SCIs on SOA formation.~~ The major role of SCIs scavengers was consuming SCIs in the reaction system, and the effect of products formed from SCIs scavengers on SCIs reactions was not expected to be important.

3.3.3 Reasons for different performances of SCIs under different RH

As a turning point of RH in SOA formation potential of SCIs was observed, which could not be explained by gas-phase reaction mechanisms, the different performances of SCIs between low- and high-humidity conditions were speculated to be due to the impact of the change of aerosol phase state on some chemical reactions. Some studies reported that the transition for the state of monoterpene-derived SOA was 65−90% RH (Bateman et al., 2015, 2016), while the transition for SOA chemical reactivity was 35−45% RH (Li et al., 2015). A similar turning point of RH in the formation of particulate dimers in monoterpene ozonolysis was reported by Kristensen et al. (2014), who observed that the concentration of dimers in particles above 50% RH was double that observed below 50% RH. In this study, with the addition of AA the acidity of aerosols would change, and some reactions that happened in bulk phase were influenced, especially under high-humidity conditions. In view of this, the effect of SOA acidity on particle-phase reactions was considered. Zhao et al. (2018) investigated the aqueous-phase hydrolysis of α-acyloxyalkyl-hydroperoxides, which were produced from reactions of SCIs and organic acids. It was found that α-acyloxyalkyl-hydroperoxides decomposed promptly when pH was larger than 5 in aqueous phase. The aqueous decomposition of α-hydroxyalkyl-hydroperoxides was also reported to be accelerated by acids, and the rate coefficients of decay increased with decreasing pH (Qiu et al., 2020a). These studies implied that acids, acting as catalysts, promoted the decomposition processes of some compounds in liquid particles and might reduce the amount of SOA. However, the effect of acidity on bulk-phase reactions was found to be complicated, and Iinuma et al. (2004) reported that acidity promoted the formation of large molecules in particles. Some reactions, which produced peroxyacetals, esters, aldols, etc., and contributed to SOA formation, could be catalyzed by acids and H^+ in aqueous phase (Ziemann and Atkinson, 2012), while the rate coefficients of these reactions with varying pH were not clear. Actually, we could not evaluate the effect of acidity on the formation of SOA accurately because the acidity of aerosols might impact a series of reactions, and the mechanisms and rates of these reactions at different pH were vague. It was noted that Chen et al. (2008) found that in the aqueous-phase ozonolysis of methacrolein and methyl vinyl ketone, the yields of products were almost independent of pH, and Zhang et al. (2009) also observed this phenomenon in the ozonolysis of α-pinene and β-pinene in aqueous phase. Thus the effect of the particle acidity on the results might also be limited here, and the accurate estimates of this issue still needed further research.

Heterogeneous reactions on aqueous aerosols impacted the formation of SOA (Knote et al., 2014; Woo et al., 2013), and here two reaction pathways were proposed. Liquid surfaces have been proven to confine SCIs into a specific orientation, which helps to maintain the stability of SCIs and provide more opportunities for SCIs to react with other species (Qiu et al., 2018a; Zhong et al., 2017). Previous studies reported that SCIs could react with a series of compounds at air-water interfaces (Heine et al., 2018; Kumar et al., 2017, 2019; Qiu et al., 2018b; Xiao et al., 2018), and some low-volatile products were observed (Enami and Colussi, 2017b, c). Under high-humidity conditions, the heterogeneous reactions of SCIs might exist with other reaction pathways of SCIs and improved the SOA formation potential of SCIs. ~~In addition,~~ On the other hand, a significant amount of H_2O_2 formed from SCIs reaction with water was observed in ozonolysis under high-humidity conditions (Chen et al., 2016; Jiang et al., 2013~~; Qiu et al., 2019~~), and water was reported to accelerate the decomposition of α-acyloxyalkyl-hydroperoxides and α-hydroxyalkyl-hydroperoxides in aqueous phase, resulting in the formation of H_2O_2 (Qiu et al., 2019, 2020b; Zhao et al., 2018).~~which might impact the aerosol-phase chemistry.~~ H_2O_2 was reported to play an important role in the nonradical oxidation of carbonyls in aqueous phase (Galloway et al., 2011; Herrmann et al., 2015), producing hydroxyhydroperoxides and promoting SOA formation (Zhao et al., 2012, 2013). The H_2O_2 oxidation of carbonyls was speculated to mainly occurr~~ed~~ in surface liquid layer of aerosols, resulting in the generation of organic peroxides and high-molecular-weight oligomers (Sui et al., 2017; Zhang et al., 2019). The impact of H_2O_2 reactions at air-liquid interface might be another reason for the performances of SCIs in SOA formation under high-humidity conditions. The inhibitory effect of water on aerosol formation in monoterpene ozonolysis was also reported by Li et al. (2019), yet they found that the RO_2-derived highly oxidized molecules (HOMs) formation was not influenced by RH, and the reason was expected to be the SCIs-derived HOMs. The main expectation of this study was to quantify the role of SCIs in SOA formation, and a limitation was the lack of measurement of aerosol composition. In ozonolysis system the detection of products formed from SCIs reactions was complicated because SCIs could react with multiple products formed from ozonolysis, and the definite reason for different SOA formation potentials of SCIs between low- and high-humidity conditions perhaps needed more composition measurements.

3.4 The contribution of limonene-derived SCIs to SOA in the atmosphere

Due to the bimolecular reactions of SCIs, SOA formation from limonene ozonolysis could be influenced by other species in the atmosphere, and to evaluate the contribution of limonene ozonolysis to SOA explicitly it is necessary to estimate the contribution of SCIs to SOA. Here three situations, forest, urban area, and indoor area, were analyzed at different RH and the concentrations of reactants were discussed as below. The concentration of limonene in tropical rainforest was reported to be about 0.18 ppbv, and in urban area 0.15 ppbv was taken as an example (Chen et al., 2010; Jia et al., 2008; Yáñez-Serrano et al., 2018). In indoor area, some studies observed high indoor limonene concentration to exceed 80 ppbv (Brown et al., 1994; Li et al., 2002), while a typical indoor concentration of limonene was considered as 2 ppbv (Mandin et al., 2017; Weschler and Carslaw, 2018). The concentrations of O_3 in forest and urban area were taken as 45 ppbv (Lelieveld et al., 2008; Williams et al., 2016). Weschler (2000) claimed that the O_3 concentration in indoor environments was 20–70% of the outdoor concentration, and 20 ppbv of O_3 was taken as a typical indoor concentration (Weschler, 2000; Weschler and Carslaw, 2018). The concentrations of some other compounds that could impact SCIs reactions, such as SO_2 and NO_2, were showed in Table S4.

To estimate the contribution of limonene-derived SCIs to SOA in the atmosphere, the concentration of SCIs needed to be calculated and the steady-state approximation was applied as Eq. (4) (Percival et al., 2013):

$$[SCI]_{ss} = \frac{k_{ozo} \cdot [O_3] \cdot [limonene] \cdot Y_{SCI}}{k_{(SCI+H2O)} \cdot [H_2O] + k_{(SCI+SO2)} \cdot [SO_2] + k_{(SCI+NO2)} \cdot [NO_2] + k_{(other)}} \qquad (4)$$

where $[SCI]_{ss}$ (molecule cm^{-3}) is the steady-state concentration of SCIs; k_{ozo} (cm^3 molecule^{-1} s^{-1}) is the rate constant of limonene reaction with O_3; $[O_3]$ (molecule cm^{-3}) is the concentration of O_3; [limonene] (molecule cm^{-3}) is the concentration of limonene; Y_{SCI} is the molar yield of SCIs; $k_{(SCI+H2O)}$ (cm^3 molecule^{-1} s^{-1}) is the rate constant of SCIs reaction with H_2O, which is 5×10^{-16} cm^3 molecule^{-1} s^{-1} as derived in this study; $[H_2O]$ (molecule cm^{-3}) is the concentration of H_2O; $k_{(SCI+SO2)}$ (cm^3 molecule^{-1} s^{-1}) is the rate constant of SCIs reaction with SO_2, which is assumed as 1×10^{-11} cm^3 molecule^{-1} s^{-1} (Lin and Chao, 2017); $[SO_2]$ (molecule cm^{-3}) is the concentration of SO_2; $k_{(SCI+NO2)}$ (cm^3 molecule^{-1} s^{-1}) is the rate constant of SCIs reaction with NO_2, which is assumed as 1×10^{-12} cm^3 molecule^{-1} s^{-1} (Lin and Chao, 2017); $[NO_2]$ (molecule cm^{-3}) is the concentration of NO_2; $k_{(other)}$ (s^{-1}) accounts for the sum of SCIs isomerization and reaction with other VOCs, and the value is also derived in the experiments. The concentrations of SCI_I and SCI_{II} were calculated seperately, and the ozonolysis of both endo-DB and exo-DB were considered. The concentrantion of SCIs was enormously affected by changing RH, and with the increase of RH to 100 % the SCIs concentration decreased to the minimum. In forest, the range of SCIs concentration varies in $2.65 \times 10^3 – 1.01 \times 10^4$ molecule cm^{-3}, and in urban and indoor area the ranges of variation are $2.15 \times 10^3 – 7.86 \times 10^3$ molecule cm^{-3} and $1.28 \times 10^4 – 4.65 \times 10^4$ molecule cm^{-3}, respectively. In forest, the typical RH is higher than 60%, and for urban and indoor area, they are usually under low-humidity conditions (Carslaw, 2017; Vereecken et al., 2012). According to the SOA formation potential of SCIs, it is estimated that ~~in all of three situations~~ the typical contribution of limonene-derived SCIs to SOA formation is $(8.21 \pm 0.15) \times 10^{-2}$ μg m^{-3} h^{-1} in forest, ~~the lowest under low-humidity conditions, where the contribution of SCIs to SOA is $(5.26 \pm 0.58) \times 10^{-2}$ μg m^{-3} h^{-1} in forest,~~ $(4.26 \pm 0.46) \times 10^{-2}$ μg m^{-3} h^{-1} in urban area, and $(2.52 \pm 0.28) \times 10^{-1}$ μg m^{-3} h^{-1} in indoor area. ~~Under high-humidity conditions, the contribution of SCIs to SOA is $(8.21 \pm 0.15) \times 10^{-2}$ μg m^{-3} h^{-1} in forest, $(6.66 \pm 0.12) \times 10^{-2}$ μg m^{-3} h^{-1} in urban area, and $(3.95 \pm 0.72) \times 10^{-1}$ μg m^{-3} h^{-1} in indoor area, which are similar to those under dry conditions.~~ As the concentrations of reactants used in experiments were higher than those in the real atmosphere, we analysed the effect of the concentrations on the results in the Supplement and confirmed the feasibility of extrapolating the results in laboratory to the ambient air.

4 Conclusions

This study investigated SOA formation of both the first- and second-generation oxidations in limonene ozonolysis at different RH, with the aim of extending our understanding of SCIs performances in SOA formation. The reaction pathways of SCIs in ozonolysis system were complex, and to figure out the role of SCIs in SOA formation, the amount of SCIs was regulated to observe the influence on SOA formation and estimate the fraction of SCIs participating in SOA formation. Results showed that SOA formation from ECIs isomerization was scarcely influenced by water, while SCIs reactions helped to explain the uncertainty of water effect on SOA formation in ozonolysis. Although part of SCIs were consumed by water, the contribution of SCIs to SOA under high-humidity conditions still resembled that obtained under dry conditions. The significant positive correlation between SOA formation and SCIs implied that the SOA formation potential of SCIs could maintain stable without obvious impact from the oxidation degree. The SOA formation potential of SCIs under high-humidity conditions was nearly double that under dry and low-humidity conditions. SOA formation from limonene ozonolysis was impacted by changing RH due to SCIs reactions, and the contribution of SCIs to SOA was needed to be considered in models even under high RH. As an important monoterpene in the atmosphere, limonene has similarities in chemical structures with its isomers, α-pinene and β-pinene. Limonene owns a similar endo-DB with α-pinene, and a similar exo-DB with β-pinene. The role of limonene-derived SCIs in SOA formation observed here might be compared with α-pinene-derived and β-pinene-derived SCIs and helped to explain the effect of water on SOA formation in ozonolysis, which was a disputable issue. In previous studies, the water effect on SOA formation in α-pinene ozonolysis was reported to be not uniform (Bonn et al., 2002; Jonsson et al., 2008; Li et al., 2019). In β-pinene ozonolysis, water was found to reduce aerosols formation under low-humidity conditions (Bonn et al., 2002; Emanuelsson et al., 2013). In this study, the performances of SCIs formed from endo-DB and exo-DB ozonolysis of limonene showed consistency. In both of the endo-DB and exo-DB oxidations, water was found to be an uncertainty on SCIs reactions and producing aerosols. ~~On the one hand, gas~~Gas-phase water consumed part of SCIs and hindered SOA formation, while~~; on the other hand,~~ condensed-phase water improved the contribution of SCIs reactions to SOA through changing the phase of aerosols and heterogeneous reactions. This study provides new insights into the role of SCIs in SOA formation from the quantitative point of view, and further studies on the high-molecular-weight products formed from SCIs are required to comprehend the role of SCIs played in the atmosphere.

Data availability. The data accessible by contacting the corresponding author (zmchen@pku.edu.cn).

Author contributions. YG designed the study, carried out the experiments, and wrote the paper. ZC helped interpret the results and modified the paper.

Competing interests. The authors declare that they have no conflict of interest.

Acknowledgments. The authors gratefully thank the National Key Research and Development Program of China (grant 2016YFC0202704) and the National Natural Science Foundation of China (grant 21477002) for financial support.

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.

Andersson-Sköld, Y. and Simpson, D.: Secondary organic aerosol formation in northern Europe: A model study, J. Geophys. Res., 106, 7357–7374, doi: 10.1029/2000JD900656, 2001.

Anglada, J. M., Aplincourt, P., Bofill, J. M., and Cremer, D.: Atmospheric formation of OH radicals and H_2O_2 from alkene ozonolysis under humid conditions, Chem. Phys. Chem., 3, 215–221, doi: 10.1002/1439-7641(20020215)3:2<215::AID-CPHC215>3.0.CO;2-3, 2002.

Aplincourt, P. and Ruiz-López, M. F.: Theoretical study of formic acid anhydride formation from carbonyl oxide in the atmosphere, J. Phys. Chem. A, 104, 380–388, doi: 10.1021/jp9928208, 2000.

Aroeira, G. J. R., Abbott, A. S., Elliott, S. N., Turney, J. M., and Schaefer III, H. F.: The addition of methanol to Criegee intermediates, Phys. Chem. Chem. Phys., 21, 17760−17771, doi: 10.1039/C9CP03480C, 2019.

Atkinson, R.: Gas-phase tropospheric chemistry of organic compounds: A review, Atmos. Environ. Part A, 24, 1–41, doi: 10.1016/j.atmosenv.2007.10.068, 1990.

Atkinson, R. and Arey, J.: Atmospheric degradation of volatile organic compounds. Chem. Rev., 103, 4605–4638, doi: 10.1021/cr0206420, 2003.

Bateman, A. P., Bertram, A. K., and Martin, S. T.: Hygroscopic influence on the semisolid-to-liquid transition of secondary organic materials, J. Phys. Chem. A, 119, 4386−4395, doi: 10.1021/jp508521c, 2015.

Bateman, A. P., Gong, Z. H., Liu, P. F., Sato, B., Cirino, G., Zhang, Y., Artaxo, P., Bertram, A. K., Manzi, A. O., Rizzo, L. V., Souza, R. A. F., Zaveri, R. A., and Martin, S. T.: Sub-micrometre particulate matter is primarily in liquid form over Amazon rainforest, Nature Geosci,. 6, 34−37, doi: 10.1038/ngeo2599, 2016.

Berndt, T., B*ö*ge, O., and Stratmann, F.: Gas-phase ozonolysis of α-pinene: gaseous products and particle formation, Atmos. Environ., 37, 3933–3945, doi: 10.1016/S1352-2310(03)00501-6, 2003.

Berndt, T., Kaethner, R., Voigtl*ä*nder, J., Stratmann, F., Pfeifle, M., Reichle, P., Sipilä, M., Kulmala, M., and Olzmann, M.: Kinetics of the unimolecular reaction of CH_2OO and the bimolecular reactions with the water monomer, acetaldehyde and acetone under atmospheric conditions, Phys. Chem. Chem. Phys., 17, 19862–19873, doi: 10.1039/C5CP02224J, 2015.

Bonn, B., Schuster, G., and Moortgat, G. K.: Influence of water vapor on the process of new particle formation during monoterpene ozonolysis, J. Phys. Chem. A, 106, 2869–2881, doi: 10.1021/jp012713p, 2002.

Bracco, L. L. B., Tucceri, M. E., Escalona, A., D*í*az-de-Mera, Y., Aranda, A., Rodr*í*guez, A. M., and Rodr*í*guez, D.: New particle formation from the reactions of ozone with indene and styrene, Phys. Chem. Chem. Phys., 21, 11214–11225, doi: 10.1039/C9CP00912D, 2019.

Brown, S. K. and Sim, M. R.: Concentrations of volatile organic compounds in indoor air – a review, Indoor Air, 4, 123–134, doi: 10.1111/j.1600-0668.1994.t01-2-00007.x, 1994.

Brune, W. H.: The chamber wall index for gas−wall interactions in atmospheric environmental enclosures, Environ. Sci. Technol., 53, 3645−3652, doi: 10.1021/acs.est.8b06260, 2019.

Cabezas, C. and Endo, Y.: Observation of hydroperoxyethyl formate from the reaction between the methyl Criegee intermediate and formic acid, Phys. Chem. Chem. Phys., 22, 446, doi: 10.1039/C9CP05030B, 2020.

Carslaw, N.: A new detailed chemical model for indoor air pollution, Atmos. Environ., 41, 1164–1179, doi: 10.1016/j.atmosenv.2006.09.038, 2007.

Chang, Y. P., Chang, H. H., and Lin, J. J. M.: Kinetics of the simplest Criegee intermediate reaction with ozone studied using a mid-infrared quantum cascade laser spectrometer, Phys. Chem. Chem. Phys., 20, 97–102, doi: 10.1039/C7CP06653H, 2018.

Chen, H. W., Ho, K. F., Lee, S. C., and Nichol, J. E.: Biogenic volatile organic compounds (BVOC) in ambient air over Hong Kong: analytical methodology and field measurement, Intern. J. Environ. Anal. Chem., 90, 988–999, doi: 10.1080/03067310903108360, 2010.

Chen, L., Wang, W. L., Wang, W. N., Liu, Y. L., Liu, F. Y., Liu, N., and Wang, B. Z.: Water-catalyzed decomposition of the simplest Criegee intermediate CH_2OO, Theor. Chem. Acc., 135, 131, doi: 10.1007/s00214-016-1894-9, 2016.

Chen, L., Huang, Y., Xue, Y. G., Shen, Z. X., Cao, J. J., and Wang, W. L.: Mechanistic and kinetics investigations of oligomer formation from Criegee intermediate reactions with hydroxyalkyl hydroperoxides, Atmos. Chem. Phys., 19, 4075–4091, doi: 10.5194/acp-19-4075-2019, 2019.

Chen, Z. M., Wang, H. L., Zhu, L. H., Wang, C. X., Jie, C. Y., and Hua, W.: Aqueous-phase ozonolysis of methacrolein and methyl vinyl ketone: a potentially important source of atmospheric aqueous oxidants, Atmos. Chem. Phys., 8, 2255–2265, doi: 10.5194/acp-8-2255-2008, 2008.

Chhantyal-Pun, R., Rotavera, B., McGillen, M, R., Khan, M. A. H., Eskola, A. J., Caravan, R. L., Blacher, L., Tew, D. P., Osborn, D. L., Percival, C. J., Taatjes, C. A., Shallcross, D. E., and Orr-Ewing, A. J.: Criegee intermediate reactions with carboxylic acids: a potential source of secondary organic aerosol in the atmosphere, ACS Earth Space Chem., 2, 833−842, doi: 10.1021/acsearthspacechem.8b00069, 2018.

Chuang, W. K. and Donahue, N. M.: Dynamic consideration of smog chamber experiment,. Atmos. Chem. Phys., 17, 10019–10036, doi: 10.5194/acp-17-10019-2017, 2017.

Criegee, R. and Wenner, G.: Die Ozonisierung des 9,10-Oklins, Liebigs Ann. Chem., 564, 9–15, doi: 10.1002/jlac.19495640103, 1949.

Drozd, G. T. and Donahue, N. M.: Pressure dependence of stabilized Criegee intermediate formation from a sequence of alkenes, J. Phys. Chem., 115, 4381–4387, doi: 10.1021/jp2001089, 2011.

Elsamra, R. M., Jalan, A., Buras, Z. J., Middaugh, J. E., and Green, W. H.: Temperature- and pressure-dependent kinetics of CH_2OO + CH_3COCH_3 and CH_2OO + CH_3CHO: direct measurements and theoretical analysis, Int. J. Chem. Kinet., 48, 474–488, doi: 10.1002/kin.21007, 2016.

Emanuelsson, E. U., Watne, A. K., Lutz, A., Ljungström, E., and Hallquist, M.: Influence of humidity, temperature, and radicals on the formation and thermal properties of secondary organic aerosol (SOA) from ozonolysis of β-pinene, J. Phys. Chem. A, 117, 10346−10358, doi: 10.1021/jp4010218, 2013.

Enami, S. and Colussi, A. J.: Criegee chemistry on aqueous organic surfaces, J. Phys. Chem. Lett., 8, 1615−1623, doi: 10.1021/acs.jpclett.7b00434, 2017a.

Enami, S. and Colussi, A. J.: Reactions of Criegee intermediates with alcohols at air−aqueous interfaces, J. Phys. Chem. A, 121, 5175−5182, doi: 10.1021/acs.jpca.7b04272, 2017b.

Enami, S. and Colussi, A. J.: Efficient scavenging of Criegee intermediates on water by surface-active cis-pinonic acid, Phys. Chem. Chem. Phys., 19, 17044−17051, doi: 10.1039/C7CP03869K, 2017c.

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, doi: 10.1021/jz100847a, 2010.

Ezell, M. J., Johnson, S. N., Yu, Y., Perraud, V., Bruns, E. A., Alexander, M. L., Zelenyuk, A., Dabdub, D., and Finlayson-Pitts, B. J.: A new aerosol flow system for photochemical and thermal studies of tropospheric aerosols, Aerosol Sci. Technol., 44, 329–338, doi: 10.1080/02786821003639700, 2010.

Faust, J. A., Wong, J. P. S., Lee, A. K. Y., and Abbatt, J. P. D.: Role of aerosol liquid water in secondary organic aerosol formation from volatile organic compounds, Environ. Sci. Technol., 51, 1405−1413, doi: 10.1021/acs.est.6b04700, 2017.

Fick, J., Pommer, L., Nilsson, C., and Andersson, B.: Effect of OH radicals, relative humidity, and time on the composition of the products formed in the ozonolysis of α-pinene, Atmos. Environ., 37, 4087–4096, doi: 10.1016/S1352-2310(03)00522-3, 2003.

Galloway, M. M., Loza, C. L., Chhabra, P. S., Chan, A. W. H., Yee, L. D. Seinfeld, J. H., and Keutsch, F. N.: Analysis of photochemical and dark glyoxal uptake: implications for SOA formation, Geophys. Res. Lett., 38, L17811, doi: 10.1029/2011GL048514, 2011.

Gong, Y. W., Chen, Z. M., and Li, H.: The oxidation regime and SOA composition in limonene ozonolysis: roles of different double bonds, radicals, and water, Atmos. Chem. Phys., 18, 15105–15123, doi: 10.5194/acp-18-15105-2018, 2018.

Hasson, A. S., Ho, A. W., Kuwata, K. T., and Paulson, S. E.: Production of stabilized Criegee intermediates and peroxides in the gas phase ozonolysis of alkenes: 2. Asymmetric and biogenic alkenes, J. Geophys. Res., 106, 34143–34153, doi: 10.1029/2001JD000598, 2001.

Hasson, A. S., Chung, M. Y., Kuwata, K. T., Converse, A. D., Krohn, D., and Paulson, S. E.: Reaction of Criegee intermediates with water vapors an additional source of OH radicals in alkene ozonolysis, J. Phys. Chem. A, 107, 6176–6182, doi: 10.1021/jp0346007, 2003.

Heine, N., Arata, C., Goldstein, A. H., Houle, F. A., and Wilson, K. R.: Multiphase mechanism for the production of sulfuric acid from SO_2 by Criegee intermediates formed during the heterogeneous reaction of ozone with squalene, J. Phys. Chem. Lett., 9, 3504−3510, doi: 10.1021/acs.jpclett.8b01171, 2018.

Herrmann, H., Schaefer, T., Tilgner, A., Styler, S. A., Weller, C., Teich, M., and Otto, T.: Tropospheric aqueous-phase chemistry: kinetics, mechanisms, and its coupling to a changing gas phase, Chem. Rev., 115, 4259–4334, doi: 10.1021/cr500447k, 2015.

Hessberg, C., Hessberg, P., Pöschl, U., Bilde, M., Nielsen, O. J., and Moortgat, G. K.: Temperature and humidity dependence of secondary organic aerosol yield from the ozonolysis of β-pinene, Atmos. Chem. Phys., 9, 3583–3599, doi: 10.5194/acp-9-3583-2009, 2009.

Hua, W., Chen, Z. M., Jie, C. Y., Kondo, Y., Hofzumahaus, A., Takegawa, N., Chang, C. C., Lu, K. D., Miyazaki, Y., Kita, K., Wang, H. L., Zhang, Y. H., and Hu, M.: Atmospheric hydrogen peroxide and organic hydroperoxides during PRIDE-PRD'06, China: their concentration, formation mechanism and contribution to secondary aerosols, Atmos. Chem. Phys., 8, 6755–6773, doi: 10.5194/acp-8-6755-2008, 2008.

Huang, H. L., Chao, W., and Lin, J. J. M.: Kinetics of a Criegee intermediate that would survive high humidity and may oxidize atmospheric SO_2, Proc. Natl. Acad. Sci., 112, 10857–10862, doi: 10.1073/pnas.1513149112, 2015.

Huang, D., Chen, Z. M., and Liang, H.: Newly observed peroxides and the water effect on the formation and removal of hydroxyalkyl hydroperoxides in the ozonolysis of isoprene, Atmos. Chem. Phys., 13, 5671–5683, doi:10.5194/acp-13-5671-2013, 2013.

Iinuma, Y., Böge, O., Gnauk, T., and Herrmann, H.: Aerosol-chamber study of the α-pinene/O_3 reaction: influence of particle acidity on aerosol yields and products, Atmos. Environ., 38, 761–773, doi: 10.1016/j.atmosenv.2003.10.015, 2004.

Jenkin, M. E.: Modelling the formation and composition of secondary organic aerosol from α- and β-pinene ozonolysis using MCM v3, Atmos. Chem. Phys., 4, 1741–1757, doi: 10.5194/acp-4-1741-2004, 2004.

Jia, C. R., Batterman, S., and Godwin, C.: VOCs in industrial, urban and suburban neighborhoods, Part 1: Indoor and outdoor concentrations, variation, and risk drivers, Atmos. Environ., 42, 2083–2100, doi: 10.1016/j.atmosenv.2007.11.055, 2008.

Jiang, L., Lan, R., Xu, Y. S., Zhang, W. J., and Yang, W.: Reaction of stabilized Criegee intermediates from ozonolysis of limonene with water: Ab Initio and DFT study, Int. J. Mol. Sci., 14, 5784–5805, doi: 10.3390/ijms14035784, 2013.

Johnson, D. and Marston, G.: The gas-phase ozonolysis of unsaturated volatile organic compounds in the troposphere, Chem. Soc. Rev., 37, 699–716, doi: 10.1039/b704260b, 2008.

Jonsson, Å. M., Hallquist, M., and Ljungström, E.: The effect of temperature and water on secondary organic aerosol formation from ozonolysis of limonene, Δ^3-carene and α-pinene, Atmos. Chem. Phys., 8, 6541–6549, doi: 10.5194/acp-8-6541-2008, 2008.

Khan, M. A. K., Morris, W. C., Galloway, M., Shallcross, B. M. A., Percival, C. J., and Shallcross, D. E.: An estimation of the levels of stabilized Criegee intermediates in the UK urban and rural atmosphere using the steady-state approximation and the potential effects of these intermediates on tropospheric oxidation cycles, Int. J. Chem. Kinet., 49, 611–621, doi: 10.1002/kin.21101, 2017.

Khan, M. A. H., Percival, C. J., Caravan, R. L., Taatjes, C. A., and Shallcross, D. E.: Criegee intermediates and their impacts on the troposphere, Environ. Sci.: Processes Impacts, 20, 437–453, doi: 10.1039/C7EM00585G, 2018.

Kim, S., Guenther, A., Lefer, B., Flynn, J., Griffin, R., Rutter, A. P., Gong, L. W., and Cevik, B. K.: Potential role of stabilized Criegee radicals in sulfuric acid production in a high biogenic VOC environment, Environ. Sci. Technol., 49, 3383−3391, doi: 10.1021/es505793t, 2015.

Kjaergaard, H. G., Kurten, T., Nielsen, L. B., Jørgensen, S., and Wennberg, P. O.: Criegee intermediates react with ozone, J. Phys. Chem. Lett., 4, 2525–2529, doi: 10.1021/jz401205m, 2013.

Knote, C., Hodzic, A., Jimenez, J. L., Volkamer, R., Orlando, J. J., Baidar, S., Brioude, J., Fast, J., Gentner, D. R., Goldstein, A. H., Hayes, P. L., Knighton, W. B., Oetjen, H., Setyan, A., Stark, H., Thalman, R., Tyndall, G., Washenfelder, R., Waxman, E. and Zhang, Q.: Simulation of semi-explicit mechanisms of SOA formation from glyoxal in aerosol in a 3-D model, Atmos. Chem. Phys., 14, 6213–6239, doi: 10.5194/acp-14-6213-2014, 2014.

Kristensen, K., Cui, T., Zhang, H., Gold, A., Glasius, M., and Surratt, J. D.: Dimers in α-pinene secondary organic aerosol: effect of hydroxyl radical, ozone, relative humidity and aerosol acidity, Atmos. Chem. Phys., 14, 4201–4218, doi: 10.5194/acp-14-4201-2014, 2014.

Kumar, M., Busch, D. H., Subramaniam, B., and Thompson, W. H.: Barrierless tautomerization of Criegee intermediates via acid catalysis, Phys. Chem. Chem. Phys., 16, 22968, doi: 10.1039/C4CP03065F, 2014a.

Kumar, M., Busch, D. H., Subramaniam, B., and Thompson, W. H.: Role of tunable acid catalysis in decomposition of hydroxyalkyl hydroperoxides and mechanistic implications for tropospheric chemistry, J. Phys. Chem. A, 118, 9701–9711, doi: 10.1021/jp505100x, 2014b.

Kumar, M., Zhong, J., Francisco, J. S., and Zeng, X. C.: Criegee intermediate-hydrogen sulfide chemistry at the air/water interface, Chem. Sci., 8, 5385–5391, doi: 10.1039/C7SC01797A, 2017.

Kumar, M., Zhong, J., Zeng, X. C., and Francisco, J. S.: Reaction of Criegee intermediate with nitric acid at the air−water interface, J. Am. Chem. Soc., 140, 4913−4921, doi: 10.1021/jacs.8b01191, 2018.

Kumar, M. and Francisco, J. S.: Elucidating the molecular mechanisms of Criegee-amine chemistry in the gas phase and aqueous surface environments, Chem. Sci., 10, 743–751, doi: 10.1039/C8SC03514H, 2019.

Lazrus, A. L., Kok, G. L., Lind, J. A., Gitlin, S. N., Heikes, B. G., and Shetter, R. E.: Automated fluorometric method for hydrogen peroxide in air, Anal. Chem., 58, 594–597, doi: 10.1021/ac00294a024, 1986.

Lee, S. and Kamens, R. M.: Particle nucleation from the reaction of a-pinene and O_3, Atmos. Environ., 39, 6822–6832, doi: 10.1016/j.atmosenv.2005.07.062, 2005.

Lee, A., Goldstein, A. H., Keywood, M. D., Gao, S., Varutbangkul, V., Bahreini, R., Ng, N. L., Flagan, R. C., and Seinfeld, J. H.: Gas-phase products and secondary aerosol yields from the ozonolysis of ten different terpenes, J. Geophys. Res., 111, D07302, doi: 10.1029/2005JD006437, 2006.

Lelieveld, J., Butler, T. M., Crowley, J. N., Dillon, T. J., Fischer, H., Ganzeveld, L., Harder, H., Lawrence, M. G., Martinez, M., Taraborrelli, D., and Williams, J.: Atmospheric oxidation capacity sustained by a tropical forest, Nature, 452, 737–740, doi: 10.1038/nature06870, 2008.

Leungsakul, S., Jaoui, M., and Kamens, R. M.: Kinetic mechanism for predicting secondary organic aerosol formation from the reaction of d-limonene with ozone, Environ. Sci. Technol., 39, 9583–9594, doi: 10.1021/es0492687, 2005.

Li, T. H., Turpin, B. J., Shields, H. C., and Weschler, C. J.: Indoor hydrogen peroxide derived from ozone/d-limonene reactions, Environ. Sci. Technol., 36, 3295–3302, doi: 10.1021/es015842s, 2002.

Li, Y. J., Liu, P. F., Gong, Z. H., Wang, Y., Bateman, A. P., Bergoend, C., Bertram, A. K., and Martin, S. T.: Chemical reactivity and liquid/nonliquid states of secondary organic material, Environ. Sci. Technol., 49, 13264−13274, doi: 10.1021/acs.est.5b03392, 2015.

Li, H., Chen, Z. M., Huang, L. B., and Huang, D.: Organic peroxides' gas-particle partitioning and rapid heterogeneous decomposition on secondary organic aerosol, Atmos. Chem. Phys., 16, 1837–1848, doi: 10.5194/acp-16-1837-2016, 2016.

Li, X. X., Chee, S., Hao, J. M., Abbatt, J. P. D., Jiang, J. K., and Smith, J. N.: Relative humidity effect on the formation of highly oxidized molecules and new particles during monoterpene oxidation, Atmos. Chem. Phys., 19, 1555–1570, doi: 10.5194/acp-19-1555-2019, 2019.

Lin, J. J. M. and Chao, W.: Structure-dependent reactivity of Criegee intermediates studied with spectroscopic methods, Chem. Soc. Rev., 46, 7483–7497, doi: 10.1039/C7CS00336F, 2017.

Liu, F., Fang, Y., Kumar, M., Thompson, W. H., and Lester, M. I.: Direct observation of vinyl hydroperoxides, Phys. Chem. Chem. Phys., 17, 20490, doi: 10.1039/c5cp02917a, 2015.

Long, B., Cheng, J. R., Tan, X. F., and Zhang, W. J.: Theoretical study on the detailed reaction mechanisms of carbonyl oxide with formic acid, J. Mol. Struct., 916,159–167, doi: 10.1016/j.theochem.2009.09.028, 2009.

Long, B., Bao, J. L., and Truhlar, D. G.: Unimolecular reaction of acetone oxide and its reaction with water in the atmosphere, Proc. Natl. Acad. Sci., 115, 6135–6140, doi: 10.1073/pnas.1804453115, 2018.

Long, B., Bao, J. L., and Truhlar, D. G.: Rapid unimolecular reaction of stabilized Criegee intermediates and implications for atmospheric chemistry, Nat. Commun., 10, 2003, doi: 10.1038/s41467-019-09948-7, 2019.

Ma, Y., Russell, A. T., and Marston, G.: Mechanisms for the formation of secondary organic aerosol components from the gas-phase ozonolysis of α-pinene, Phys. Chem. Chem. Phys., 10, 4294–4312, doi: 10.1039/b803283a, 2008.

Mandin, C., Trantallidi, M., Cattaneo, A., Canha, N., Mihucz, V. G., Szigeti, T., Mabilia, R., Perreca, E., Spinazzѐ, A., Fossati, S., Kluizenaar, Y. D., Cornelissen, E., Sakellaris, I., Saraga, D., Hӓnninen, O., Fernandes, E. D. O., Ventura, G., Wolkoff, P., Carrer, P., and Bartzis, J.: Assessment of indoor air quality in office buildings across Europe – The OFFICAIR study, Sci. Total Environ., 579, 169−178, doi: 10.1016/j.scitotenv.2016.10.238, 2017.

Matsuoka, K., Sakamoto, Y., Hama, T., Kajii, Y., and Enami, S.: Reactive uptake of gaseous sesquiterpenes on aqueous surfaces, J. Phys. Chem. A, 121, 810−818, doi: 10.1021/acs.jpca.6b11821, 2017.

Mauldin III, R. L., Berndt, T., Sipilä, M., Paasonen, P., Petäjä, T., Kim, S., Kurtén, T., Stratmann, F., Kerminen, V. M., and Kulmala, M.: A new atmospherically relevant oxidant of sulphur dioxide, Nature, 488, 193–197, doi: 10.1038/nature11278, 2012.

McGillen, M. R., Curchod, B. F. E., Chhantyal-Pun, R., Beames, J. M., Watson, N., Khan, M. A. H., McMahon, L., Shallcross, D. E., and Oee-Ewing, A. J.: Criegee intermediate−alcohol reactions, a potential source of functionalized hydroperoxides in the atmosphere, ACS Earth Space Chem., 1, 664−672, doi: 10.1021/acsearthspacechem.7b00108, 2017.

McVay, R. C., Cappa, C. D., and Seinfeld, J. H.: Vapor-wall deposition in chambers: theoretical considerations, Environ. Sci. Technol., 48, 10251–10258, doi: 10.1021/es502170j, 2014.

McVay, R. C., Zhang, X., Aumont, B., Valorso, R., Camredon, M., La, Y. S., Wennberg, P. O., and Seinfeld, J. H.: SOA formation from the photooxidation of α-pinene: systematic exploration of the simulation of chamber data, Atmos. Chem. Phys., 16, 2785–2802, doi: 10.5194/acp-16-2785-2016, 2016.

Mutzel, A., Rodigast, M., Iinuma, Y., Bӧge, O., and Herrmann, H.: Monoterpene SOA — Contribution of first-generation oxidation products to formation and chemical composition, Atmos. Environ., 130, 136–144, doi: 10.1016/j.atmosenv.2015.10.080, 2016.

Nah, T., McVay, R. C., Zhang, X., Boyd, C. M., Seinfeld, J. H., and Ng, N. L.: Influence of seed aerosol surface area and oxidation rate on vapor wall deposition and SOA mass yields: a case study with α-pinene ozonolysis, Atmos. Chem. Phys., 16, 9361–9379, doi: 10.5194/acp-16-9361-2016, 2016.

Nah, T., McVay, R. C., Pierce, J. R., Seinfeld, J. H., and Ng, N. L.: Constraining uncertainties in particle-wall deposition correction during SOA formation in chamber experiments, Atmos. Chem. Phys., 17, 2297–2310, doi: 10.5194/acp-17-2297-2017, 2017.

Newland, M. J., Rickard, A. R., Sherwen, T., Evans, M. J., Vereecken, L., Munoz, A., Rodenas, M., and Bloss, W.: The atmospheric impacts of monoterpene ozonolysis on global stabilised Criegee intermediate budgets and SO_2 oxidation: experiment, theory and modelling, Atmos. Chem. Phys., 18, 6095–6120, doi: 10.5194/acp-18-6095-2018, 2018.

Ng, N. L., Kroll, J. H., Keywood, M. D., Bahreini, R., Varutbangkul, V., Flagan, R. C., Seinfeld, J. H., Lee, A., and Goldstein, A. H.: Contribution of first- versus second-generation products to secondary organic aerosols formed in the oxidation of biogenic hydrocarbons, Environ. Sci. Technol., 40, 2283–2297, doi: 10.1021/es052269u, 2006.

Osborn, D. L. and Taatjes, C. A.: The physical chemistry of Criegee intermediates in the gas phase, Int. Rev. Phys. Chem., 34, 309–360, doi: 10.1080/0144235X.2015.1055676, 2015.

Palm, B. B., Sá, S. S., Day, D. A., Campuzano-Jost, P., Hu, W. W., Seco, R., Sjostedt, S. J., Park, J.-H., Guenther, A. B., Kim, S., Brito, J., Wurm, F., Artaxo, P., Thalman, R., Wang, J., Yee, L. D., Wernis, R., Isaacman-VanWertz, G., Goldstein, A. H., Liu, Y. J., Springston, S. R., Souza, R., Newburn, M. K., Alexander, M. L., Martin, S. T., and Jimenez, J. L.: Secondary organic aerosol formation from ambient air in an oxidation flow reactor in central Amazonia, Atmos. Chem. Phys., 18, 467–493, doi: 10.5194/acp-18-467-2018, 2018.

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.

Percival, C. J., Welz, O., Eskola, A. J., Savee, J. D., Osborn, D. L., Topping, D. O., Lowe, D., Utemne, S. R., Bacak, A., Figgans, G. M., Cooke, M. C., Xiao, P., Archibald, A. T., Jenkin, M. E., Derwent, R. G., Piipinen, I., Mok, D. W. K., Lee, E. P. F., Dyke, J. M., Taatjes, C. A., and Shallcross, D. E.: Regional and global impacts of Criegee intermediates on atmospheric sulphuric acid concentrations and first steps of aerosol formation, Faraday Discuss., 165, 45–73, doi: 10.1039/c3fd00048f, 2013.

Qiu, J. T., Ishizuka, S., Tonokura, K., Colussi, A. J., and Enami, S.: Reactivity of monoterpene Criegee intermediates at gas−liquid interfaces, J. Phys. Chem. A, 122, 7910−7917, doi: 10.1021/acs.jpca.8b06914, 2018a.

Qiu, J. T., Ishizuka, S., Tonokura, K., and Enami, S.: Reactions of Criegee intermediates with benzoic acid at the gas/ liquid interface, J. Phys. Chem. A, 122, 6303−6310, doi: 10.1021/acs.jpca.8b04995, 2018b.

Qiu, J. T., Ishizuka, S., Tonokura, K., Colussi, A., and Enami, S.: Water dramatically accelerates the decomposition of α-hydroxyalkyl-hydroperoxides in aerosol particles, J. Phys. Chem. Lett., 10, 5748−5755, doi: 10.1021/acs.jpclett.9b01953, 2019.

Qiu, J. T., Tonokura, K., and Enami, S.: Proton-catalyzed decomposition of α-hydroxyalkyl-hydroperoxides in water, Environ. Sci. Technol., 54, 10561–10569, doi: 10.1021/acs.est.0c03438, 2020a.

Qiu, J. T., Liang, Z. C., Tonokura, K., Colussi, A. J., and Enami, S.: Stability of monoterpene-derived α-hydroxyalkyl-hydroperoxides in aqueous organic media: relevance to the fate of hydroperoxides in aerosol particle phases, Environ. Sci. Technol., 54, 3890−3899, doi: 10.1021/acs.est.9b07497, 2020b.

Renbaum-Wolff, L., Grayson, J. W., Bateman, A. P., Kuwata, M., Sellier, M., Murray, B. J., Shilling, J. E., Martin, S. T., and Bertram, A. K.: Viscosity of α-pinene secondary organic material and implications for particle growth and reactivity, Proc. Natl. Acad. Sci., 110, 8014–8019, doi: 10.1073/pnas.1219548110, 2013.

Riipinen, I., Pierce, J. R., Yli-Juuti, T., Nieminen, T., Häkkinen, S., Ehn, M., Junninen, H., Lehtipalo, K., Petäjä, T., Slowik, J., Chang, R., Shantz, N. C., Abbatt, J., Leaitch, W. R., Kerminen, V.-M., Worsnop, D. R., Pandis, S. N., Donahue, N. M., and Kulmala, M.: Organic condensation: a vital link connecting aerosol formation to cloud condensation nuclei (CCN) concentrations, Atmos. Chem. Phys., 11, 3865–3878, doi: 10.5194/acp-11-3865-2011, 2011.

Saathoff, H., Naumann, K.-H., Möhler, O., Jonsson, Å. M., Hallquist, M., and Schurath, U.: Temperature dependence of yields of secondary organic aerosols from the ozonolysis of α-pinene and limonene, Atmos. Chem. Phys., 9, 1551–1577, doi: 10.5194/acp-9-1551-2009, 2009.

Sakamoto, Y., Inomata, S., and Hirokawa, J.: Oligomerization reaction of the Criegee intermediate leads to secondary organic aerosol formation in ethylene ozonolysis, J. Phys. Chem. A, 117, 12912−12921, doi: 10.1021/jp408672m, 2013.

Sakamoto, Y., Yajima, R., Inomata, S., and Hirokawa, J.: Water vapour effects on secondary organic aerosol formation in isoprene ozonolysis, Phys. Chem. Chem. Phys., 19, 3165–3175, doi: 10.1039/C6CP04521A, 2017.

Sander, W.: Carbonyl oxides—rising stars in tropospheric chemistry, Angew. Chem. Int. Ed., 53, 362–364, doi: 10.1002/anie.201305736, 2014.

Sheps, L., Scully, A. M., and Au, K.: UV absorption probing of the conformer-dependent reactivity of a Criegee intermediate CH_3CHOO, Phys. Chem. Chem. Phys., 16, 26701–26706, doi: 10.1039/C4CP04408H, 2014.

Shiraiwa, M. and Seinfeld, J. H.: Equilibration timescale of atmospheric secondary organic aerosol partitioning, Geophys. Res. Lett., 39, L24801, doi: 10.1029/2012GL054008, 2012.

Shu, Y. H. and Atkinson, R.: Rate constants for the gas phase reactions of O_3 with a series of terpenes and OH radical formation from the O_3 reactions with sesquiterpenes at 296 ± 2 K, Int. J. Chem. Kinet., 26, 1193–1205, doi: 10.1002/kin.550261207, 1994.

Sipilä, M., Jokinen, T., Berndt, T., Richters, S., Makkonen, R., Donahue, N. M., Mauldin III, R. L., Kurtén, T., Paasonen, P., Sarnela, N., Ehn, M., Junninen, H., Rissanen, M. P., Thornton, J., Stratmann, F., Herrnann, H., Worsnop, D. R., Kulmala, M., Kerminen, V.-M., and Petäjä, T.: Reactivity of stabilized Criegee intermediates (sCIs) from isoprene and monoterpene ozonolysis toward SO_2 and organic acids, Atmos. Chem. Phys., 14, 12143–12153, doi: 10.5194/acp-14-12143-2014, 2014.

Sui, X., Zhou, Y. F., Zhang, F., Chen, J. M., Zhu, Z. H., and Yu, X. Y.: Deciphering the aqueous chemistry of glyoxal oxidation with hydrogen peroxide using molecular imaging, Phys. Chem. Chem. Phys., 19, 20357–20366, doi: 10.1039/C7CP02071F, 2017.

Taatjes, C. A., Meloni, G., Selby, T. M., Trevitt, A. J., Osborn, D. L., Percival, C. J., and Shallcross, D. E. J.: Direct observation of the gas-phase Criegee intermediate (CH_2OO), Am. Chem. Soc., 130, 11883−11885, doi: 10.1021/ja804165q, 2008.

Taatjes, C. A., Welz, O., Eskola, A. J., Savee, J. D., Scheer, A. M., Shallcross, D. E., Rotavera, B., Lee, E. P. F., Dyke, J. M., Mok, D. K. W., Osborn, D. L., and Percival, C. J.: Direct measurements of conformer-dependent reactivity of the Criegee intermediate CH_3CHOO, Science, 340, 177–180, doi: 10.1126/science.1234689, 2013.

Taatjes, C. A., Shallcross, D. E., and Percival, C. J.: Research frontiers in the chemistry of Criegee intermediates and tropospheric ozonolysis, Phys. Chem. Chem. Phys., 16, 1704–1718, doi: 10.1039/c3cp52842a, 2014.

Taatjes, C. A.: Criegee Intermediates: What direct production and detection can teach us about reactions of carbonyl oxides, Annu. Rev. Phys. Chem., 68, 183–207, doi: 10.1146/annurev-physchem-052516-050739, 2017.

Tadayon, S. V., Foreman, E. S., and Murray, C.: Kinetics of the reactions between the Criegee intermediate CH_2OO and alcohols, J. Phys. Chem. A, 122, 258−268, doi: 10.1021/acs.jpca.7b09773, 2018.

Tillmann, R., Hallquist, M., Jonsson, Å. M., Kiendler-Scharr, A., Saathoff, H., Iinuma, Y., and Mentel, Th. F.: Influence of relative humidity and temperature on the production of pinonaldehyde and OH radicals from the ozonolysis of α-pinene, Atmos. Chem. Phys., 10, 7057–7072, doi: 10.5194/acpd-10-3129-2010, 2010.

Tu, P. J. and Johnson, M. V.: Particle size dependence of biogenic secondary organic aerosol molecular composition, Atmos. Chem. Phys., 17, 7593–7603, doi: 10.5194/acp-17-7593-2017, 2017.

Veghte, D. P., Altaf, M. B., and Freedman, M. A.: Size dependence of the structure of organic aerosol, J. Am. Chem. Soc., 135, 16046–16049, doi: 10.1021/ja408903g, 2013.

Vereecken, L., Harder, H., and Novelli, A.: The reaction of Criegee intermediates with NO, RO_2, and SO_2, and their fate in the atmosphere, Phys. Chem. Chem. Phys., 14, 14682–14695, doi: 10.1039/c2cp42300f, 2012.

Vereecken, L., Richard, A. R., Newland, M. J., and Bloss, W. J.: Theoretical study of the reactions of Criegee intermediates with ozone, alkylhydroperoxides, and carbon monoxide, Phys. Chem. Chem. Phys., 17, 23847–23858, doi: 10.1039/c5cp03862f, 2015.

Warren, B., Malloy, Q. G. J., Yee, L. D., and Cocker III, D. R.: Secondary organic aerosol formation from cyclohexene ozonolysis in the presence of water vapor and dissolved salts, Atmos. Environ., 43, 1789–1795, doi: 10.1016/j.atmosenv.2008.12.026, 2009.

Watson, N. A. I., Black, J. A., Stonelake, T. M., Knowles, P. J., and Beames, J. M.: An extended computational study of Criegee intermediate−alcohol reactions, J. Phys. Chem. A, 123, 218−229, doi: 10.1021/acs.jpca.8b09349, 2019.

Welz, O., Savee, J. D., Osborn, D. L., Vasu, S. S., Percival, C. J., Shallcross, D. E., and Taatjes, C. A.: Direct kinetic measurements of Criegee intermediate (CH_2OO) formed by reaction of CH_2I with O_2, Science, 335, 204–207, doi: 10.1126/science.1213229, 2012.

Weschler, C. J.: Ozone in indoor environments: concentration and chemistry, Indoor Air, 10, 269–288, doi: 10.1034/j.1600-0668.2000.010004269.x, 2000.

Weschler, C. J. and Carslaw, N.: Indoor chemistry, Environ. Sci. Technol., 52, 2419−2428, doi: 10.1021/acs.est.7b06387, 2018.

Williams, J., Keβel, S. U., N𝑜̈lscher, A. C., Yang, Y. D., Lee, Y., Y𝑎́𝑛̃ez-Serrano, A. M., Wolff, S., Kesselemeier, J., Kl𝑢̈pfel, T., Lelieveld, J., and Shao, M.: Opposite OH reactivity and ozone cycles in the Amazon rainforest and megacity Beijing: Subversion of biospheric oxidant control by anthropogenic emissions, Atmos. Environ., 125, 112–118, doi: 10.1016/j.atmosenv.2015.11.007, 2016.

Wilson, J., Imre, D., Beranek, J., Shrivastava, M., and Zelenyuk, A.: Evaporation kinetics of laboratory-generated secondary organic aerosols at elevated relative humidity, Environ. Sci. Technol., 49, 243–249, doi: 10.1021/es505331d, 2015.

Winterhalter, R., Neeb, P., Grossmann, D., Kolloff, A., Horie, O., and Moortgat, G.: Products and mechanism of the gas phase reaction of ozone with β-pinene, J. Atmos. Chem, 35, 165–197, doi: 10.1023/A:1006257800929, 2000.

Woo, J. L., Kim, D. D., Schwier, A. N., Li, R. Z., and McNeill, V. F.: Aqueous aerosol SOA formation: impact on aerosol physical properties, Faraday Discuss., 165, 357–367, doi: 10.1039/C3FD00032J, 2013.

Xiao, P., Yang, J. J., Fang, W. H., and Cui, G. L.: QM/MM studies on ozonolysis of α-humulene and Criegee reactions with acids and water at air–water/acetonitrile interfaces, Phys. Chem. Chem. Phys., 20, 16138−16150, doi: 10.1039/C8CP01750F, 2018.

Y𝑎́𝑛̃ez-Serrano, A. M., N𝑜̈lscher, A. C., Bourtsoukidis, E., Alves, E. G., Ganzeveld, L., Bonn, B., Wolff, S., Sa, M., Yamasoe, M., Williams, J., Andreae, M. O., and J𝑢̈rgen, K.: Monoterpene chemical speciation in a tropical rainforest: variation with season, height, and time of day at the Amazon Tall Tower Observatory (ATTO), Atmos. Chem. Phys., 18, 3403–3418, doi: 10.5194/acp-18-3403-2018, 2018.

Yao, L., Ma, Y., Wang, L., Zheng, J., Khalizov, A., Chen, M. D., Zhou, Y. Y., Qi, L., and Cui, F. P.: Role of stabilized Criegee Intermediate in secondary organic aerosol formation from the ozonolysis of α-cedrene, Atmos. Environ., 94, 448–457, doi: 10.1016/j.atmosenv.2014.05.063, 2014.

Ye, Q., Robinson, E. S., Ding, X., Ye, P. L., Sullivan, R. C., and Donahue, N. M.: Mixing of secondary organic aerosols versus relative humidity, Proc. Natl. Acad. Sci., 113, 12649–12654, doi: 10.1073/pnas.1604536113, 2016.

Ye, J. H., Abbatt, J. P. D., and Chan, A. W. H.: Novel pathway of SO_2 oxidation in the atmosphere: reactions with monoterpene ozonolysis intermediates and secondary organic aerosol, Atmos. Chem. Phys., 18, 5549–5565, doi: 10.5194/acp-18-5549-2018, 2018.

Yu, K. P., Lin, C. C., Yang, S. C., and Zhao, P.: Enhancement effect of relative humidity on the formation and regional respiratory deposition of secondary organic aerosol, J. Hazard. Mater., 191, 94–102, doi: 10.1016/j.jhazmat.2011.04.042, 2011.

Zhang, J. Y., Hartz, K. E. H., Pandis, S. N., and Donahue, N. M.: Secondary organic aerosol formation from limonene ozonolysis: homogeneous and heterogeneous influences as a function of NO_x, J. Phys. Chem. A, 110, 11053–11063, doi: 10.1021/jp062836f, 2006.

Zhang, X., Chen, Z. M., Wang, H. L., He, S. Z., and Huang, D. M.: An important pathway for ozonolysis of alpha-pinene and beta-pinene in aqueous phase and its atmospheric implications, 43, 4456–4471, doi: 10.1016/j.atmosenv.2009.06.028, 2009.

Zhang, X., Cappa, C. D., Jathar, S. H., McVay, R. C., Ensberg, J. J., Kleeman, M. J., and Seinfeld, J. H.: Influence of vapor wall loss in laboratory chambers on yields of secondary organic aerosol, P. Natl. Acad. Sci. USA, 111, 5802–5807, doi: 10.1073/pnas.1404727111, 2014.

Zhang, X., Schwantes, R. H., McVay, R. C., Lignell, H., Coggon, M. M., Flagan, R. C., and Seinfeld, J. H.: Vapor wall deposition in Teflon chambers, Atmos. Chem. Phys., 15, 4197–4214, doi: 10.5194/acp-15-4197-2015, 2015.

Zhang, F., Yu, X. F., Chen, J. M., Zhu, Z. H., and Yu, X. Y.: Dark air–liquid interfacial chemistry of glyoxal and hydrogen peroxide, NPJ Clim. Atmos. Sci., 2, 28, doi: 10.1038/s41612-019-0085-5, 2019.

Zhao, R., Lee, A. K. Y., and Abbatt, J. P. D.: Investigation of aqueous-phase photooxidation of glyoxal and methylglyoxal by aerosol chemical ionization mass spectrometry: observation of hydroxyhydroperoxide formation, J. Phys. Chem. A, 116, 6253–6263, doi: 10.1021/jp211528d, 2012.

Zhao, R., Lee, A. K. Y., Soong, R., Simpson, A. J., and Abbatt, J. P. D.: Formation of aqueous-phase alpha-hydroxyhydroperoxides (α-HHP): potential atmospheric impacts, Atmos. Chem. Phys., 13, 5857–5872, doi: 10.5194/acp-13-5857-2013, 2013.

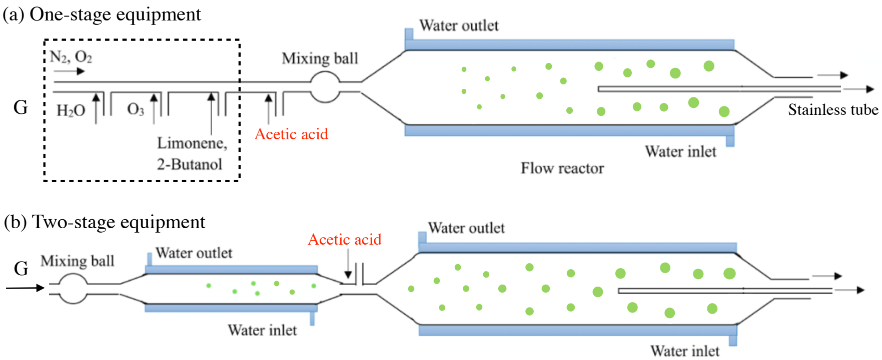
Zhao, R., Kenseth, C. M., Huang, Y. L., Dalleska, N. F., Kuang, X. M., Chen, J. R., Paulson, S. E., and Seinfeld, J. H.: Rapid aqueous-phase hydrolysis of ester hydroperoxides arising from Criegee intermediates and organic acids, J. Phys. Chem. A, 122, 5190−5201, doi: 10.1021/acs.jpca.8b02195, 2018.

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.

Zhong, J., Kumar, M., Zhu, C. Q., Francisco, J. S., and Zeng, X. C.: Surprising stability of larger Criegee intermediates on aqueous interfaces, Angew. Chem. Int. Ed., 56, 7740–7744, doi: 10.1002/anie.201702722, 2017.

Zhong, J., Kumar, M., Francisco, J. S., and Zeng, X. C.: Insight into chemistry on cloud/aerosol water surfaces, Acc. Chem. Res., 51, 1229−1237, doi: 10.1021/acs.accounts.8b00051, 2018.

Ziemann, P. J. and Atkinson, R.: Kinetics, products, and mechanisms of secondary organic aerosol formation, Chem. Soc. Rev., 41, 6582–6605, doi: 10.1039/C2CS35122F, 2012.



835

Figure 1: Diagram of the experimental setup. The (a) one-stage and (b) two-stage apparatuses are used to investigate the first- and second-generation oxidation. The green circles represent the process of SOA growth.

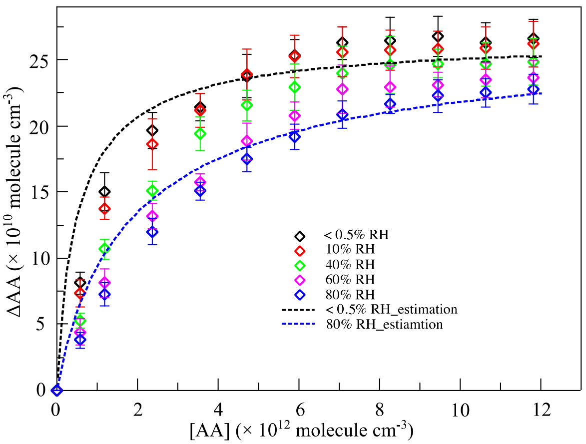
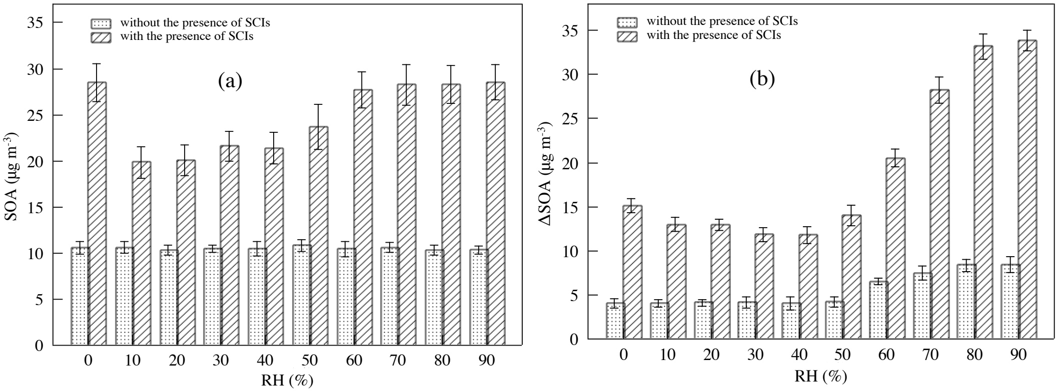


Figure 2: The variations of the consumption of acetic acid (ΔAA) with the concentration of acetic acid ([AA]) at different relative humidity (RH) in the first-generation oxidation. Scatters: measured ΔAA; Black line: estimated ΔAA at < 0.5% RH; Blue line: estimated ΔAA at 80% RH.



845 **Figure 3: Impact of the presence of SCIs on (a) SOA mass concentration (SOA) in the first-generation oxidation and (b) the increment of SOA mass concentration (ΔSOA) in the second-generation oxidation at different relative humidity (RH).**

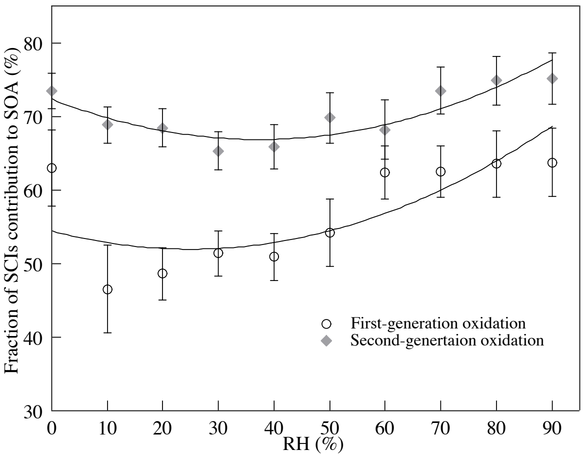


Figure 4: The fraction of SCIs reactions contributing to SOA formation in the (a) first- and (b) second-generation oxidation at different relative humidity (RH).

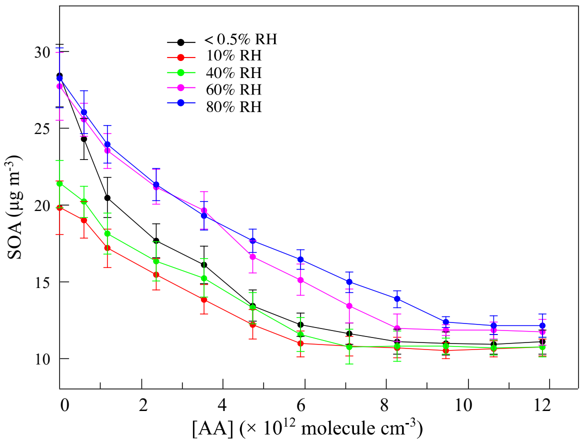


Figure 5: The variation of SOA mass concentration (SOA) with the concentration of acetic acid ([AA]) at different relative humidity (RH) in the first-generation oxidation.

855

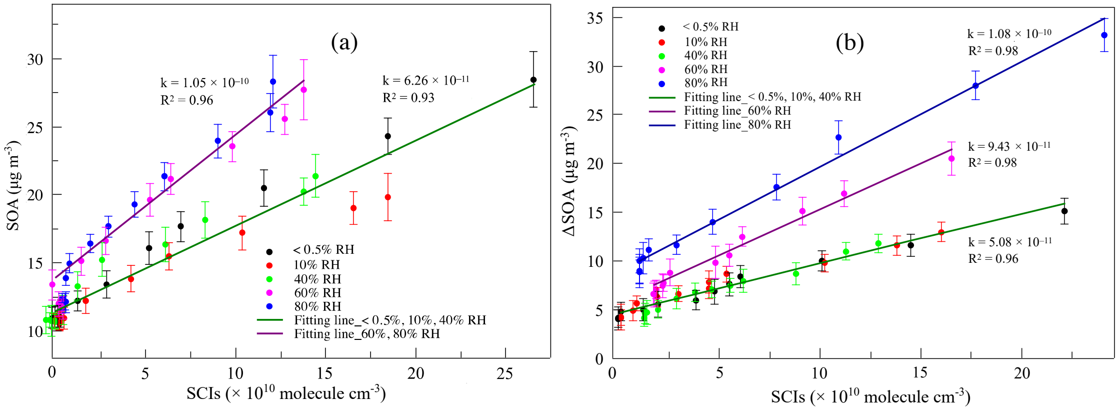


Figure 6: (a) The dependence of SOA mass concentration (SOA) on the amount of SCIs at different relative humidity (RH) in the first-generation oxidation. (b) The dependence of SOA mass concentration increment (ΔSOA) on the amount of SCIs at different relative humidity (RH) in the second-generation oxidation.

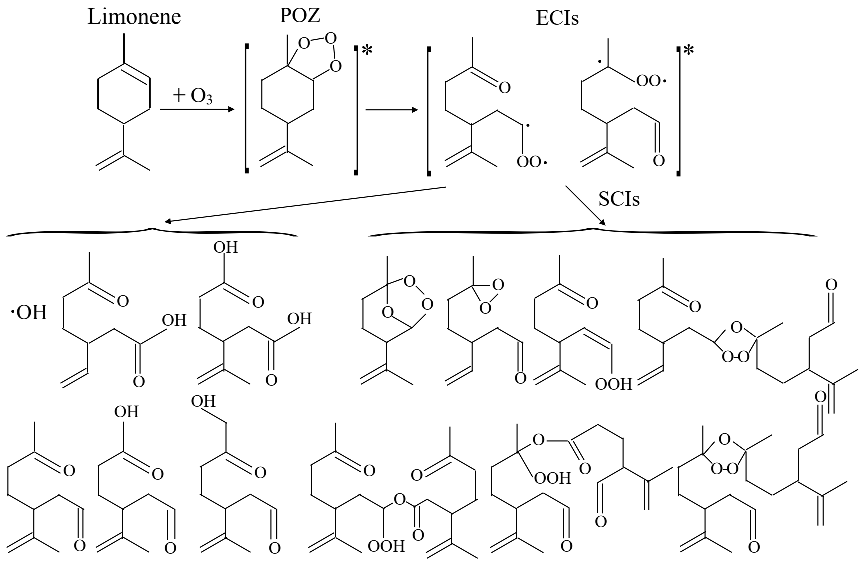


Figure 7: Reaction scheme of limonene ozonolysis.