

Interactive comment on “Quantification of the role of stabilized Criegee intermediates in the formation of aerosols in limonene ozonolysis” by Yiwei Gong and Zhongming Chen

Anonymous Referee #1

Received and published: 26 August 2020

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.

Specific Comments: 1. I am most concerned about the side reaction of SCIs with 2-

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butanol. In page 10, the authors wrote “The rate constants of CH₂OO reaction with methanol and ethanol were measured to be about 10⁻¹⁵ 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 $k \sim 10^{-13}$ cm³ molecule⁻¹ s⁻¹ for CH₂OO + CH₃OH/C₂H₅OH and $k \sim 4 \times 10^{-14}$ cm³ molecule⁻¹ s⁻¹ for (CH₃)₂CCOO + CH₃OH at ~ 298 K. Furthermore, Tadayon et al. (J. Phys. Chem. A 2018, 122, 1, 258–268) reported the rate constants of $(1.9 \pm 0.5) \times 10^{-13}$ 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 10⁻¹⁵ cm³ molecule⁻¹ s⁻¹ seems to be inadequate. If the authors assumed the rate constant to be 10⁻¹³ 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.

2. 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?

3. 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.

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