

Atmos. Chem. Phys. Discuss., referee comment RC1
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Review of acp-2021-199

Anonymous Referee #2

Referee comment on "Role of Criegee intermediates in the formation of sulfuric acid at a Mediterranean (Cape Corsica) site under influence of biogenic emissions" by Alexandre Kukui et al., Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2021-199-RC1>, 2021

Review of "Role of Criegee intermediates in the formation of sulfuric acid at a Mediterranean (Cape Corsica) site under influence of biogenic emissions"

This study focuses on the investigation of the H₂SO₄ budget in a remote coastal environment by using measured H₂SO₄ and OH radical with a CIMS instrument. The study investigates whether SCI have an impact in the H₂SO₄ formation for this environment and finds that they contribute to less than 10% to the H₂SO₄ during day and up to 40% during the night. 50% of the H₂SO₄ observed during the night cannot be explained.

The paper is well written and well structured and makes use of the most up to date literature values for the SCI chemistry to assess their impact on the H₂SO₄ formation. It extensively discusses the relatively large uncertainties that pertains to both the SCI, the loss rate for H₂SO₄ as well as the uncertainties on the rate coefficient between OH and SO₂. The latter I find rather interesting as the discrepancies with available (and recommended) rates are large and introduce a big bias when trying to investigate additional sources for the H₂SO₄.

I recommend publication after the following comments are considered.

Specific comments:

Check the formatting of the citations. Often it is formatted wrongly when in the text (especially in the SI).

Please add the page number to the SI.

Page 2, Line 45: I do not understand the sentence "...a noticeable fraction of nucleation mode particle's growth..."

Page 3, Line70: together with the formation of a SCI there is always the formation of a carbonyl compound.

Page 4, Lines 102-103: There is experimental evidence that the formation of SO_3 from the reaction of SCI from β -pinene and SO_2 is pretty much immediate (Ahrens et al., 2014) so that I would think there is not much doubt about it also for larger SCI.

Page 4, Line 110: I would also add the reference to the paper by Novelli et al. (2017) which came up with a similar estimate from measured data.

Section 2.2.1. Please be careful in the definition of ROx. Is it $\text{OH} + \text{HO}_2 + \text{RO}_2$ or is the OH contribution removed? Later on (page 6 line 176 and 181), I assume, ROx becomes RO_2 but that is a big difference. Was the HO_2 contribution removed from the ROx signal or this is a typo? If the CIMS can separate between HO_2 and RO_2 it would be interesting to shortly clarify this.

Page 9, Line 275: Isn't the value of OH measured at night lower than the stated detection limit of $5 \times 10^5 \text{ cm}^{-3}$? How meaningful is the nighttime analysis then?

Page 12, Line 318: It is stated that the reaction between OH and SO_2 under estimate the H_2SO_4 concentration at night. Although this is clearly visible in figure 2a, I am not so convinced it is clear from figure 1 where I have the feeling that overall the H_2SO_4 is well explained by the OH radical as in the night often the H_2SO_4 calculated from OH is missing or has some sharp low values which might bias the median profile shown in figure 2a. What is the cause for the sharp low values for the H_2SO_4 calculated from $\text{OH} + \text{SO}_2$ in figure 1?

Page 14, Line 352: which instead of what

Page 15, Figure 5a: Shouldn't the difference between the measured H_2SO_4 and the H_2SO_4 calculated from the contribution of the OH radical always be higher or equal to the H_2SO_4 calculated from the SCI? Also, it looks relatively stable over the whole day...more as if affected by some scaling factor than additional chemistry. Once considering all the

different uncertainties I am not so sure that I would conclude the abstract stating that SCI are an important source of H_2SO_4 in SCI rich environments. Also, as the reaction with acids (which is fast) is not included as a loss rate for the SCI, what described here is an upper limit.

Page 18, Lines 455-457: I am not sure I follow here. If the lower rate coefficient for $\text{OH} + \text{SO}_2$ as proposed by (Blitz et al., 2017a, 2017b), shouldn't the contribution of SCI to the formation of H_2SO_4 increase substantially?

Reference

Ahrens, J., Carlsson, P. T., Hertl, N., Olzmann, M., Pfeifle, M., Wolf, J. L., and Zeuch, T.: Infrared detection of Criegee intermediates formed during the ozonolysis of beta-pinene and their reactivity towards sulfur dioxide, *Angew Chem Int Ed Engl*, 53, 715-719, doi:10.1002/anie.201307327, 2014.

Blitz, M. A., Salter, R. J., Heard, D. E., and Seakins, P. W.: An Experimental Study of the Kinetics of $\text{OH}/\text{OD}(v=1,2,3) + \text{SO}_2$: the Limiting High Pressure Rate Coefficients as a Function of Temperature, *The Journal of Physical Chemistry A*, doi:10.1021/acs.jpca.7b01294, 2017a.

Blitz, M. A., Salter, R. J., Heard, D. E., and Seakins, P. W.: An Experimental and Master Equation Study of the Kinetics of $\text{OH}/\text{D} + \text{SO}_2$: The Limiting High Pressure Rate Coefficients, *The Journal of Physical Chemistry A*, doi:10.1021/acs.jpca.7b01295, 2017b.

Novelli, A., Hens, K., Tatum Ernest, C., Martinez, M., Nölscher, A. C., Sinha, V., Paasonen, P., Petäjä, T., Sipilä, M., Elste, T., Plass-Dülmer, C., Phillips, G. J., Kubistin, D., Williams, J., Vereecken, L., Lelieveld, J., and Harder, H.: Estimating the atmospheric concentration of Criegee intermediates and their possible interference in a FAGE-LIF instrument, *Atmos. Chem. Phys.*, 17, 7807-7826, doi:10.5194/acp-17-7807-2017, 2017.

