

Atmos. Chem. Phys. Discuss., referee comment RC3
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Comment on acp-2021-199

Anonymous Referee #4

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-RC3>, 2021

Kukui et al. investigate the potential contribution of Criegee intermediates to sulfuric acid formation in the western Mediterranean, via analysis of field measurements from the ChArMEx project. Two chemical pathways to sulfuric acid are considered: reaction of OH with SO₂ (+ H₂O + O₂), and the reactions of stabilized (thermalized) Criegee intermediates (SCIs) with SO₂. Using their measurements of OH and unsaturated VOCs, Kukui et al. estimate the contribution of each channel to measured sulfuric acid and determine that reaction of SCIs with SO₂ contribute ~10% of daytime and ~40% of nighttime sulfuric acid. While this analysis closes the daytime budget for sulfuric acid, ~50% of the nighttime sulfuric acid concentration remains unaccounted for. The authors conclude that SCI chemistry may be an important nighttime sulfuric acid source for VOC-rich environments.

This is a timely and interesting study that is suitable for publication in ACP. Some comments, questions, and suggestions follow.

- The reaction of MACR-oxide with SO₂ has also recently been measured (Lin et al., Chemistry Communications, 2021).
- To what extent do you anticipate that an inability to quantify all unsaturated VOCs with your field instrument could be contributing to the significant unexplained nighttime sulfuric acid? One way to explore this could be through comparison of calculated vs. measured OH reactivity. For example, if you compare measured [VOC] to measured OH reactivity, do you have significant underprediction of OH reactivity that could be rationalized by higher [unsaturated VOC] than you were able to quantify in the field?
- What parameters from the literature do you use to calculate the concentration of the water dimer vs. monomer?
- The layout of Figure 3 (positioning of inset figures) makes this figure confusing to look at.
- In section 4.2., the phrasing where you describe the work of Vereecken et al. (that

uses the Blitz et al. rate constants) is somewhat confusing – please rephrase for clarity.

- I would also suggest stating somewhere that there are, inevitably, large uncertainties in the rate coefficients for the reaction of SO₂ with more complex SCI that have not yet been directly measured or calculated.
- In Table S5, it is noted that the experimental results of Caravan et al. suggest faster unimolecular decomposition of Z-MVK-oxide in better agreement with the results of Vereecken et al. This is not correct – Caravan et al. actually suggest that faster decay rate in their experiments could be due to internal excitation of anti-MVK-oxide and/or a low yield of stabilized anti-MVK-oxide – both of which are experimental factors.