

Interactive comment on “Atmospheric isoprene ozonolysis: impacts of stabilized Criegee intermediate reactions with SO₂, H₂O and dimethyl sulfide” by M. J. Newland et al.

Anonymous Referee #2

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General: This is an interesting contribution on a chamber-based study of Criegee radicals derived from isoprene (ISO) and their reactivity towards SO₂, water and DMS.

As the reaction of ISO with ozone is known to be slow, it might be expected that the ISO-CIs will not play a very important role in gas phase chemistry.

These systems under study are very complex when the role of the Criegee radical is to be investigated starting from ozonolysis experiments. It cannot be excluded that products formed after ozonolysis will also establish sinks for the Criegee intermediates and that the sinks for the CIs can really be ascribed to the processes the study of which

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was intended.

The final suggestion that the reaction of ISO-SCIs with DMS could be important should be viewed with care.

Overall, the manuscript clearly warrants publication.

Details / Specific comments:

1) Experiments have been conducted with fairly high initial reactant mixing ratios (isoprene: 400 ppbv, ozone: 500 ppbv, cyclohexane for OH scavenging: 75 ppmv) and 25% isoprene conversion, i.e. oxidation product generation from ozonolysis and OH reaction in the order of a few 10¹² molecules cm⁻³. Only small information is given regarding the SCI reaction with the oxidation products (carbonyls, acids) in competition with the reactions with SO₂ and H₂O / DMS depending on reaction time (progress of isoprene conversion). Data analysis considers a fixed, free parameter “L” for additional SCI loss steps. The authors should provide more information how the consecutive reactions of products with SCI could influence their findings especially for low H₂O / DMS concentrations. Maybe, a modelling study could be helpful.

2) SCI + H₂O: Ozone and SO₂ measurements, applied in data analysis, have been done with the help of corresponding monitors. What was the reason for the limited RH range of 0.5 – 27%? Atmospheric conditions exceed this range clearly. A wider range would give more experimental information to allow distinguishing between the H₂O monomer and dimer reaction.

3) Kinetic approach: Did the authors use an initial rate approach and the smoothed fitting procedure served as a tool to generate $\Delta\text{SO}_2/\Delta\text{O}_3$ at $t = 0$? Please give a more precise explanation! (It is also important in connection with point 1.) What kind of fitting function was used?

4) SCI + DMS: The finding of a rate coefficient close to collision limit could be very important for atmospheric chemistry. This rate coefficient was derived from an indirect

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way of determination using four runs only. The data show a large scattering, cf. Figure 6. The authors should discuss possible errors of k_8 in detail.

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