

Interactive comment on “Measurement-model comparison of stabilized Criegee Intermediate and Highly Oxygenated Molecule production in the CLOUD chamber” by Nina Sarnela et al.

Anonymous Referee #1

Received and published: 26 October 2017

The authors present measurements of highly oxidised molecules (HOMs) and sulfuric acid (H₂SO₄) using chemical ionization atmospheric pressure interface time-of-flight (CI-API-TOF) mass spectrometry in α -pinene ozonolysis experiments in the CLOUD chamber at CERN. The data are used in conjunction with model calculations to infer yields of HOMs and stabilized Criegee intermediates (sCI), which, in the presence of the OH radical scavenger H₂, are assumed to be responsible for the observed production of H₂SO₄.

The experiments, and analyses of the observations, are challenging, and the manuscript will be of interest to the atmospheric science community. However, I have

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a number of comments listed below which ought to be addressed prior to publication, notably relating to the treatment of uncertainties and comparisons made between measurements and model simulations without any quantification.

Comments:

Page 1, line 9: Comma after ‘Douglas’.

Page 1, line 34: Remove ‘the’ in ‘... through the ozonolysis...’.

Page 2, line 1: What do the authors mean by the term ‘dynamic model’? A kinetic model, or simply calculation of expected production rates, might be a better description.

Page 2, line 1: Remove ‘the’ in ‘... for the HOM formation...’.

Page 2, line 2: Please be clear which measured concentrations the model is fit to – sCI concentrations have not been measured directly.

Page 2, line 4: Please quantify ‘faster than simulated’.

Page 2, line 11: Remove ‘a’ in ‘... can act as a cloud...’.

Page 2, line 12: Replace ‘have’ with ‘has’ in ‘A lot of effort have been...’.

Page 2, lines 28-30 and elsewhere: There is an inconsistency in the use of ‘f’ and ‘ph’ in the spellings for sulfur compounds. IUPAC recommend ‘sulfur’ over ‘sulphur’ and the authors should at least be consistent in their choice for all S compounds throughout the manuscript.

Page 2, line 33: The Mauldin III et al. reference does not explicitly demonstrate the reaction of sCI + SO₂, but rather it is inferred as a possible explanation for their measurements.

Page 2, line 35: ‘collision stabilized’ to ‘collisionally stabilized’. Is the 2011 reference the most appropriate? There was an awareness of this behaviour prior to 2011.

Page 3, line 10: Please be clear which compound you are referring to in ‘...in which

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the compound is ...'. Perhaps something along the lines of '... in which the radical(s) produced after the initial oxidation are...'.
Page 3, line 10,13&elsewhere : Please be consistent is in use of 'oxidized' or 'oxidised'.

Page 3, line 13: Perhaps insert 'intramolecular' before 'H-shift'? It is not clear whether this mechanism was introduced by Ehn et al. as it has been known for many years in combustion chemistry.

Page 3, line 16: 'oxidixed'.

Page 3, line 20: Reactions of RO \dot{A} ñ2 with NO, RO2 and HO2 do not always form closed shell products.

Page 3, line 25: Remove 'the' in '... at least in the forested regions...'.
Page 4, Table 1: CLOUD description 'residence'.

Page 4, line 21: The temperature stability seems extremely accurate for such a large volume. How is this achieved? Can the authors be sure there are no temperature gradients? A stability of 0.05 K is perhaps possible for the cooling system used for the chamber, but seems rather accurate for the entire volume of the chamber itself.

Page 5, line 8: Please consider changing 'cutting'.
Page 5, line 9: 'formed particles' to 'particles formed'.
Page 6, line 5: Is there an additional space before C6H8O7?
Page 6, line 13: What are the uncertainties in the calibration coefficients?

Page 7: Please provide some more details regarding the previous determinations of k(HOM), k(SA) and T(SA)/T(HOM). Given HOMs are a wide range of species, how representative is the value of k(HOM) determined experimentally? What are the ranges reported for k(HOM) and k(SA)? Are these upper and lower limits? What were the mean values and uncertainties? The statement that the rates are 'close to each other'

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assumes that k(HOM) and k(SA) are each at the same point in their range, which is not necessarily the case. How would the results from this work be impacted if one were at its upper limit and the other at its lower limit? Please also provide further details on how the systematic uncertainties in H2SO4 and HOM concentrations were estimated, how these uncertainties compare to the simulations presented in Figures 4&5 and how the determinations of the yields are affected.

Page 8, lines 3-7: Was a yield term required to calculate the production of sCI? What are the references for the temperature-dependent rate coefficients? Are they also Atkinson et al. (2006)?
Page 8, line 7: 'is competed' to 'in competition with'.
Page 8, line 9: Is there any evidence for reaction with the water dimer?
Page 8, lines 16: Are the reaction parameters referred to those given in lines 25 & 26?
Page 8, lines 17-18: Which 'other compound' does this refer to? The sCI reaction partner? Is this relevant for discussion of reaction with SO2 or water?
Page 8, lines 20-22: Please consider some additional brackets in the equations.
Page 9, line 1: Please consider changing 'minima and maxima' to 'lower and upper limits' if this is what is being reported.
Page 10, line 9: Can the 'low' concentrations of contaminants be quantified?
Page 12, Figure 2: Are the data shown in (b) included in Figures 4&5? Is it necessary to reproduce the plots? Inclusion of the model simulations in Figures 4&5 make is more informative than the data shown in Figure 2.
Page 12, line 13: Can the statement 'formed right after RO2' be quantified? How soon is 'right after'?
Page 14, line 16: Quantify 'fast'.

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Page 14, line 18: What was the expectation based on? If this uses model simulations can these be shown?

Page 14, line 24: Is there a closing parenthesis missing?

Page 14, line 32: Remove 'to' following '...relatively high for ...'.

Page 15, Figure 4: Which parameters were varied in the fitted simulation?

Page 15, line 3: Is the hyphen needed in '-chamber'?

Page 15, line 11: Quantify 'slightly higher'.

Page 16, lines 1&7&22: Quantify the terms 'matched perfectly', 'increased significantly' and 'reproduce the measured concentrations very well'.

Page 16, line 11: Is there a full stop missing at the end of the sentence?

Page 17, Figure 5: What does the colour in the plot represent that isn't listed in the legend? Is it the overlap between the simulations using Ehn results with those of Jokinen? Uncertainty in the fit? Which parameters were fitted?

Page 18, line 21: Which reaction parameters specifically? What is meant by 'broader modelling'?

References: Several formatting issues (e.g. page 19 line 19, page 20, line 11) and with subscripts.

Interactive comment on Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2017-780>, 2017.