

Interactive comment on “Acid-yield measurements of the gas-phase ozonolysis of ethene as a function of humidity using Chemical Ionisation Mass Spectrometry (CIMS)” by K. E. Leather et al.

Anonymous Referee #1

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General comments

This manuscript describes experiments aimed measuring the formic acid yield from the ozonolysis of ethene as a function of relative humidity (RH). The authors employ an environmental chamber reactor and use chemical ionisation mass spectrometry to detect the formic acid product. The work appears to resolve discrepancies in the formic acid yields measured in previous low RH experiments, while confirming the strong RH dependence overall of the formic acid yields. The work also places constraints on rate constant for the reaction of the stabilised Criegee biradical (CB) with water. Based on these results, the authors suggest that the reaction of stabilised CB with water

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will dominate the production of formic acid on a global scale. Because current global models underpredict formic acid concentrations, the work addresses a topical issue and is quite appropriate for ACP.

For the most part, the work has been carefully planned and executed, and the analysis is logical. However, there are some missing details that the authors should consider before preparing a final version of the manuscript.

1) Further discussion of the lack of detection sensitivity for HMHP. Since the authors attempted the detection of HMHP, they obviously agree that its detection would've been very useful in the validation of the proposed mechanism. It does seem as if the I-ionisation scheme should work for HMHP; if true, the lack of detection would raise the thorny issue of some kind of heterogenous loss mechanism. Therefore, I think it is reasonable to address the CIMS detection issue in some more detail. Are there reasons to suspect that I- scheme wouldn't work for HMHP? Along the same lines, I'm surprised the authors didn't try the CF₃O⁻ chemical ionisation method, which has been used to detect HMHP by others (such as Wennberg's group). Are there reasons why the CF₃O⁻ scheme couldn't be used in this system?

2) Inclusion of the fate of hot CB in the mechanism. I agree with the interactive comment by J.-F. Müller from 26 October concerning the inclusion of the fate of hot CB in the mechanism. The current mechanism given in Figure 9 does not accurately reflect the expectation that the decomposition of hot CB is a major product pathway for the ozonolysis of ethene. As Müller points out, the inclusion of this aspect simply requires the slight readjustment of the reported k_3/k_2 ratio.

3) More detailed discussion of the assumptions used in the global formic acid yield predictions. I would suggest that authors include a more detailed discussion of the predicted formic acid yields from isoprene and its oxidation products (to which the present results are directly applicable, as opposed to some of the monoterpenes). Since isoprene dominates the global formic acid production, it makes more sense to

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discuss this case in more detail.

Specific issues:

p 25175, line 12, typo: “with” should be replaced with “and”

p 25175, line 26, addition: add “radiative” between “indirect” and “forcing”

p 25176, line 6, suggestion: replace “resulting from “ with “due to”

p 25177, line 3, sentence fragment: add period at the end of the parenthetical statement and make start new sentence with “Here . . .”

p 25181, line 24, possible error: Is the formic acid sensitivity really about 0.1 ppt?

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 25173, 2011.

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