

## ***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 #2**

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The manuscript describes the measurement of formic acid yields from the ozonolysis of ethene, with emphasis on the application of these yields in a global chemical transport model to estimate the importance of ozonolysis as a source of formic acid globally. Formic acid, along with several other products, are measured using Chemical Ionization Mass Spectrometry (CIMS) with the iodide anion as the ionizing agent. The experimental method and CIMS measurement is verified by good agreement between the measured ethene-ozone rate constant and the accepted literature values. Applying the RH dependence of formic acid yields measured here to both ethene and isoprene, ozonolysis may account for greater than half of global formic acid sources, with the rest coming from sources such as direct emission and OH processing. Using a simple

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model for Criegee intermediate reaction, the rate constant for  $\text{CI} + \text{H}_2\text{O}$  is estimated to be between  $1.5 \cdot 10^{-12}$  and  $1.5 \cdot 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ .

This work follows the authors' previous contributions to understanding gas phase ozonolysis. The current results are important for understanding both the detailed physical chemistry of alkene ozonolysis and the importance of its mechanistic details on a global scale. Clearly this work is of merit to the journal and the atmospheric chemistry community, but several critical discussion points must be clarified and/or altered prior to publication.

Before further discussion (and given prior ACP discussion), two points should be clearly stated : 1) Only stabilized Criegee intermediates (SCI) have been *proposed capable* of bi-molecular reaction. (Hatakeyama 1984, Niki 1987, Chew and Atkinson 1996, Wolff 1997, Neeb and Moortgart 1999, Kroll2001a, Kroll 2001b, Anglada 2002, Presto 2004, Orzechowska 2005, Johnson and Marston 2008, Donahue 2011, Tillman 2011, Drozd 2011a, Beck 2011, Alam 2011) 2) It seems that the geometry of an SCI may be critical in determining its lifetime with respect to isomerization/decomposition (Marston and Johnson 2008, Kuwata 2010, Drozd 2011b). SCI may be formed with the COO moiety pointing towards the substituted (syn) or unsubstituted (anti) side of the SCI. This leads to a nomenclature issue, in that the CI, in terms of a resonance model, has both bi-radical and zwitterionic character, with the zwitterionic form and its double bond character creating a barrier to syn/anti isomerization. Though some electronic structure studies have shown the importance of one or the other form, it seems that there is evidence of a structure that will in any event create a barrier for conversion between the syn- and anti-CI forms (Cremer 1979, Anglada 1996, Johnson and Marston 2008, Taatjes 2008, Kuwata 2010) It may be best termed simply the Criegee intermediate, which implies some superposition of both structural forms. This same point about structure was discussed in a recent paper by the authors. (Taatjes et al. last paragraph of pg. 11884)

1) I agree with the first reviewer that more detail should be given concerning the global

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formic acid yields from isoprene. These assumptions have been stated in the current ACPD discussion, and this clarification should be included in the revised text.

"We find that the HCOOH yield per CH<sub>2</sub>O formed is between 0.65 and 0.8." (Oct 31) It is confusing that in the model the formic acid yields can be above 0.4, when in your experiments the formic acid yields level off at a value of 0.4. This discrepancy should be explained, because it seemed that the implication of your own experimental evidence was that 0.4 was roughly the maximum yield for formic acid from H<sub>2</sub>COO. ("The formic acid yield appears to increase from RH ≤ 30% although between 20-30% RH there is a levelling off.") The reason for the leveling off would presumably be that you have titrated all the available SCI. Because of the disparate lifetimes of Cl\* and SCI, the required increase in humidity to react with Cl\* would be far beyond 100% RH. Finally, the formic acid yield (if all is assumed to be formed from SCI + H<sub>2</sub>O) should be applied only to the fraction of SCI formed (see below). These inconsistencies should be addressed before the model results can be meaningfully interpreted.

2) Humidity should only affect the fate of SCI. Any unstabilized ("hot") Cl\* should isomerize/decompose far too rapidly to react in a bi-molecular fashion. This has consistently been the working understanding in all the publications mentioned in the first point of clarification above. This is also how the Univ. of Leeds Master Chemical Mechanism treats ozonolysis (e.g. α-pinene). The previous response by the authors concerning using a single rate constant (or a sum of rate constants) for Cl\* and SCI decomposition (if this is the intended interpretation) is at odds with all the listed publications, which all separate the behavior of Cl\* and SCI, as in Presto 2004 (R5) and the MCM. During thermalization with the bath gas, the Cl\* and SCI become separate, distinct populations. The rate constant for loss of Cl\* (which is itself dynamic during thermalization) would only apply for the very short time while thermalization takes place (nsec), after thermalization the SCI decomposition rate constant would be applied to the remaining SCI. The SCI yield in these experiments seems to be in the range of 40% (if fully titrated by H<sub>2</sub>O at RH = 30%). Alam et al. report slightly higher SCI yields of 54%. It seems this may change the derived rate constant for SCI+H<sub>2</sub>O by perhaps a factor

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of 2 ( $\sim 1/Y_{SCI}$ ), which does not greatly affect major conclusions. It should be made clear that the ratio  $k_3/k_2$  corresponds to competing rates for SCI reaction. This will be important for future comparisons with different alkenes that have different SCI yields and different rates for SCI + H<sub>2</sub>O.

3) The influence of RH is interesting in this system, given that we might expect SCI yields to be low due to the small size of ethene. The availability for H<sub>2</sub>COO from ethene ozonolysis to react with water may be strongly related to the fact that it forms only anti-SCI. The recent, very detailed, calculations of Kuwata et al. indicate that anti-SCI may readily react with water and that this process can compete with isomerization at relevant RH conditions. Some discussion of the role of the H<sub>2</sub>COO geometry (only anti-SCI) in its reactivity with water could be added.

4) Some comparison concerning the recent results of Tillman et al. and Alam et al., which concern humidity dependent product yields from ozonolysis, might be useful in building a broader context to the effect of humidity on ozonolysis product yields and SCI formation from H<sub>2</sub>COO.

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