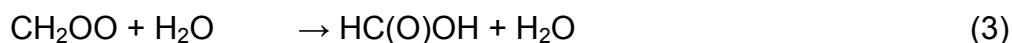


We again thank J.F. Muller for his further “reactions” to our replies. We hope that these comments will fully answer his questions. We have not made the model analysis carried out clear enough it would seem. We have carried out experimental studies on the ozonolysis of ethene and derived a relationship for the removal of CH<sub>2</sub>OO in this system based on the two reactions, denoted in the manuscript as



A simple model encapsulating these two reactions (3) and (4) is used to derive a value for the ratio  $k_4/k_3$  ( $=3.3 \times 10^{17}$  molecule cm<sup>-3</sup>) and hence the yield can be retrieved from the equation

$$\text{HCOOH}_{\text{yield}} = \frac{k_3[\text{H}_2\text{O}]}{k_3[\text{H}_2\text{O}] + k_4} \quad (5)$$

So, we explicitly allow for ‘decomposition’ that is not reaction with water in the form of reaction (4). We then model sources of CH<sub>2</sub>OO from other systems such as isoprene, methyl vinyl ketone and methacrolein. In the literature, during isoprene ozonolysis, CH<sub>2</sub>OO is a co-product when both methacrolein and methyl vinyl ketone are formed. Although there is some variability between experimental studies, adopting a value of 0.6 for the yield of methacrolein and methyl vinyl ketone combined is reasonable. Therefore, for every isoprene undergoing ozonolysis, 0.6 CH<sub>2</sub>OO will be formed. We then use the ratio  $k_4/k_3$  and equation (5) to determine the yield of HCOOH from the CH<sub>2</sub>OO formed, as a function of [H<sub>2</sub>O] in the model. Given that the bulk of isoprene emissions (and hence MACR and MVK formed from rapid secondary production of isoprene) are located in the tropics where temperature and humidity are high, we find that the HCOOH yield per CH<sub>2</sub>OO formed is between 0.65 and 0.8. Given that the yield of CH<sub>2</sub>OO from isoprene ozonolysis is ~ 0.6, this then produces HCOOH yields relative to isoprene removed via ozonolysis of between approximately 0.4 – 0.5. These values are indeed higher than those derived by Neeb et al., and Hasson of ~ 0.3. However, at infinite [H<sub>2</sub>O], reaction (3) must dominate totally and it follows that as [H<sub>2</sub>O] increases so reaction (3) must become more important. In our analysis we have assumed that the analysis of CH<sub>2</sub>OO decomposition from ethene can be applied to CH<sub>2</sub>OO decomposition following its production from other ozonolysis systems.

We assume that J.F. Muller is referring to Kroll et al., JPCA, 2001, 105, 4446-4457. Within the manuscript, specifically referring to ozonolysis of ethene it states that “Still, much of the carbonyl oxide is formed vibrationally “cold” and cannot undergo prompt unimolecular dissociation”. Whilst the master equations are performed up to 1000 Torr, experimental results are performed at 10 and 100 Torr and are focused on OH yields rather than formic acid production. Nevertheless, our results do not ignore the decomposition of CB, quite the contrary; we implicitly take it into account. Our simple analytical solution looks at the mass balance of the reaction, i.e. the yield is the total

amount of formic acid produced relative to the total amount of alkene lost. The unimolecular decomposition rate of CB that we include is the total decomposition (i.e. both Hot and SCI). i.e.



As both are first order losses, then the overall first order loss rate  $k_{\text{tot}} = k_4 + k_6$ . This does not change the form equation or our conclusions. If the total CB decomposition rate was increased then the retrieved rate of reaction with water would have to increase to match the experimental yields. As we state in the original manuscript “Clearly it is not possible to obtain a unique fit to the experimental data” we then discuss the range of both decomposition rates considered. We are happy to add a line in the manuscript to say that the decomposition rate constant includes both HOT and SCI decomposition to remove any perceived confusion. We do state that “an upper limit on the decomposition rate of the Criegee bi-radical of  $5 \times 10^7 \text{ s}^{-1}$ ” can be set, this corresponds to a lifetimes of 20 ns, which is prompt. Clearly if we increase the decomposition rate in our experimental system we will have to increase the rate coefficient via reaction with  $\text{H}_2\text{O}$ . This will INCREASE the atmospheric importance of the reaction. However, we have set reasonable limits within the manuscript. Unfortunately, up to this date, it has been impossible to experimentally differentiate HCOOH yield from vibrationally hot or Stabilized carbonyl oxide. Again we, and all previous studies, are determining the total yield of HCOOH from ozonolysis of ethene.

In terms of the atmospheric model and hence atmospheric implications, we have included both a decomposition rate of CB and a reaction with  $\text{H}_2\text{O}$  by using the ratio and yield as described earlier. Indeed, Donahue et al., 2011 (PCCP, **13**, 10848-10857) states that “We have tantalizing evidence that we can achieve complete stabilization at 100 Torr pressure of SCI compounds starting from C12–C14 precursors” Whilst the review focuses on OH yields and not formic acid production it is clear that it is possible to produce SCIs. The lifetimes with respect to decomposition have been suggested to be 100 ms, i.e. reaction with  $\text{H}_2\text{O}$  could easily compete with decomposition within the atmosphere. So for biogenic compounds, with a terminal alkene bond our postulated HCOOH source could be important.

As we state in our manuscript and original reply. We are not claiming that there is evidence for HCOOH formation. However, we are stating that ozonolysis produces more organic acids on a molecule by molecule basis compared to reaction with OH. Which, makes clear mechanistic sense and verified by *Larsen relative to Glasius et al.* We are using this to hypothesize that ozone will make more formic acid than reaction with OH. Indeed, this also makes mechanistic sense, as outlined in the references that J.F.Muller provides.

With reference to the Fenske et al., paper. The work assumes a decomposition rate of the Criegee radical and infers a loss rate of SCI via titration with aldehydes. Indeed, they state that their retrieved rate coefficients

are dependent of the decomposition rate assumed. It is not clear to us that vibrationally hot CI would not react with aldehydes too. We are, to the best of our knowledge, unaware of any direct experimental evidence that could prove this either way. Our previous work represents the first studies to directly measure the Criegee radicals (Taatjes et al., 2008) in the gas phase, as of yet there are no direct studies of Criegee radical reactions in the literature. Our current study narrows the large range in CB + H<sub>2</sub>O rate coefficients and our modeling studies look at the implications of these results.

Finally, our agreement with previous studies is not just 'above 20% RH'. We agree within experimental error with all studies across the RH studied other than that of Orzechowska and Paulson. This is clearly shown by the error bars within figure 6 and the reported errors in tables 1 and 2. So we are unclear as to what the comment "It is correct that the experimental results obtained by Leather et al. agree to a large extent with previous studies. In particular, the HCOOH yield at > 20% RH" refers to when we agree within error with studies under "dry" conditions.