We would like to thank the referees for their comments on the manuscript and give detailed responses where appropriate.

Referee 1

1. HMHP could not be seen via I- detection. The ionization scheme is very well suited for acids and proceeds via I- adduct formation. HMHP does not possess an acid group and thus could explain why we would not observe HMHP. Attempts were made to change the ionization scheme, (using NF_3-, CF_3O- and SF_6-) however, I- signal dominated the mass spectrum even after 1 week, so we could not utilize other schemes. However, the synthesis of HMHP was verified by the appearance of an absorption band at 950-1075 cm^{-1} Bauerle (1999), Minkoff (1953) using FTIR analysis.

2. The referee also asks us to include a section on the formation of so called Hot Criegee intermediates.

The carbonyl oxide produced in ozonolysis of ethene will be produced with a Boltzmann distribution of vibrational energies. The Creigee radical is assumed to be ‘HOT’ when there is enough vibrational energy to overcome the energy barrier to unimolecular decomposition. The CB is considered to be ‘stablized” (or a SCI) if it has energies below this energy barrier. There are no direct experimental measurements of the vibrational energy distribution of the Criegee radicals. However, experimentally the fraction of SCI is assigned via titration reactions and assuming a different reactivity between the HOT CB and SCI. In a theoretical study Kroll et al., 2001 state that much (~50%) of the carbonyl oxide from the ethene system is formed vibrationally “cold”. Indeed, Donahue et al., 2011 (PCCP, **13**, 10848-10857) suggest that for C_2-C_{15} precursors all CB can be completely stabilised at 100 Torr. One can imagine two different scenarios for CB formation

Scenario 1

If we imagine that all the Criegee biradicals are in a stabilised form in this system then it is possible to model the HC(O)OH yield as a function of RH. We assume that the Criegee radical has one of two fates, reaction with H_2O to form HC(O)OH (reaction 3) or decomposition (possibly wall loss) independent of H_2O. This model can be summarised by the two reactions

$CH_2OO + H_2O \rightarrow HC(O)OH + H_2O$ (3)

$CH_2OO \rightarrow$ products (4)

A simple model encapsulating these two reactions (3) and (4) is compared with measurement data in Figure 7. Here, the yield of HC(O)OH is defined as

$$HCOOHyield = \frac{k_3[H_2O]}{k_3[H_2O]+k_4} \quad (5)$$

Clearly it is not possible to obtain a unique fit to the experimental data as there are no direct measurements of the rate of reaction of the Criegee radical with water (k_3). Indeed, estimates for the reaction rate of the Criegee radical with water range over three orders of magnitude (Calvert et al., 2000). However, a ratio between k_3 and k_4 emerges, where k_4/k_3 is 3.3×10^{17} molecule cm^{-3} to obtain an excellent fit to the measurement data. Assuming that k_3 has a maximum value of around 1.5×10^{-10} cm^3 $molecule^{-1}$ s^{-1} (gas kinetic limit) this puts an upper limit on the decomposition rate of the stabilised Criegee bi-radical of 5×10^7 s^{-1}, similarly, if k_3 is around 1.5×10^{-17} cm^3 $molecule^{-1}$ s^{-1} as suggested by indirect measurements then k_4 is only 5 s^{-1}, much lower than theoretical (e.g. Ryzhkov and Ariya, 2004) estimates. Indeed, the work of Ryzhkov and Ariya (2004) suggest a value of k_4 between 5×10^5 s^{-1} and 5 $\times10^2$ s^{-1}, which provides a range for k_3 of 1.5×10^{-12} cm^3 $molecule^{-1}$ s^{-1} – 1.5×10^{-15} cm^3 $molecule^{-1}$ s^{-1}.

Scenario 2

If we imagine that all the Criegee biradicals are in an unstabilised ('Hot') form in this system then it is also possible to model the HC(O)OH yield as a function of RH. Following the work of Kroll et al., (2001a; 2001b), we note that for unstabilised CH_2OO biradicals, the dominant fate is to isomerise to dioxirane which can then rearrange to form HC(O)OH in a vibrationally excited state, the so called 'hot acid' channel. This hot acid can either be stabilised (here by water as well as the bath gas) or decompose to form OH. A similar model analysis can be proposed where reaction (6) involves stabilisation of the hot acid and reaction (7) its decomposition

$HC(O)OH^* + H_2O \rightarrow HC(O)OH + H_2O$ (6)

$HC(O)OH^* \rightarrow$ products (7)

Hence we arrive at a similar expression for the yield of HC(O)OH

$$HCOOHyield = \frac{k_6[H_2O]}{k_6[H_2O] + k_7} \tag{8}$$

Once again it is not possible to obtain a unique fit to the experimental data as there are no direct measurements of either k_6 or k_7. However, a ratio between k_6 and k_7 as in scenario **1** means that k_7/k_6 is 3.3×10^{17} molecule cm^{-3} to obtain an excellent fit to the measurement data. Since k_6 represents a collision rate it is reasonable to estimate it to be around 1.5×10^{-10} cm^3 molecule^{-1} s^{-1} (gas kinetic limit) which provides a value for the decomposition rate of the unstabilised Criegee bi-radical of approximately 5×10^7 s^{-1}.

A variety of experiments and theoretical investigations suggest that between 35% - 54% (Alam et al., 2010) of the CH_2OO formed are stabilised and one assumes that the rest must be unstabilised. The production of OH, believed to arise predominantly from unstabilised CH_2OO is reported to be between 0- 22% of all Criegee biradicals formed (Alam et al., 2010). Data from this work suggests that the yield of HC(O)OH is at least 40% and indeed is still increasing at the highest water vapour investigated. Hence, if the lower estimates for the fraction of stabilised CH_2OO are correct (~ 35-40%), then HC(O)OH must also be formed from unstabilised CH_2OO, presumably via quenching of the 'hot acid'.

Hence, current research suggests that scenario **1** could represent up to about 54% of CH_2OO formed. If we assume that all the observed HC(O)OH is from this channel only and that the maximum yield is 0.54, then k_4/k_3 is ~ 1 $\times 10^{17}$ molecule cm^{-3} and the value for k_3 is larger still than estimated in scenario **1**, although this study cannot provide a unique value. Can scenario **2** exist? If the lowest evaluations of the amount of stabilised CH_2OO are correct, then it would appear that stabilisation is occurring at atmospheric pressure with the increasing relative humidity. Indeed, at 'high pressures' stabilisation must occur, although there is considerable debate as to the value required to approach this high pressure limit. There is further support from the result of Alam et al., (2010) who report a decrease in radical yield with increased RH, i.e. the stabilised Criegee radical is being removed via reaction with water. In an analogous system, the ozonolysis of alpha pinene, Tillmann et al., (2010) report an increase in the yield of pinonaldehyde as a result of the increased titration of the SCI with water. The result of Tillmann et al., would suggest the reaction of SCI with water is a ubiquitous phenomenon with far reaching implications for tropospheric chemistry.

3. The atmospheric implications/modeling section has been extended to include the implications of the two different model scenarios and the implications of Y_{SCI}. Regardless of the approach the formation of the HCOOH is increased using our new rate data. Using the yields of CH_2OO from the work of Aschmann et al., (1996) and Grosjean et al., (1993), the yield of CH_2OO is between 0.85-0.95 and even assuming that the fraction that produces HC(O)OH is 0.52 yields around 4.3 Tg/yr, and assuming a fraction of up to 0.8 yields around 6.7 Tg/year.

All the minor typographical errors have been addressed

Referee 2

1. We have addressed the point with regard to the vibrational excitation of CB in our response to referee 1. It should be noted that in the work of Allam et al., 2011 where they look at the formation of radicals as a function of RH, that their radical yield decreases with RH, which is in agreement with this work, i.e. the addition of water leads to the formation of stable species.

2. Clearly for the Carbonyl oxide CH_2OO anti and syn isomers do not exist as a consequence of symmetry and will have no impact on our interpretation of HCOOH yields.

3. The referee is correct that the reactivity of anti isomer can be orders of magnitude faster than that of the syn isomer. In this present study we do not take this into account given the range in the VOC mix and the range in reactivity (over three orders of magnitude) we feel that this is beyond the scope of the current paper. Furthermore, in general the CRI model lumps isomeric radicals together.

4. The referee is correct that the HC(O)OH will only level off at infinite water. Clearly from our mathematical approach the increase in HCOOH as function of RH will reduce. Our use of loose language added to the confusion and has now been removed for the sake of clarity. Furthermore, we have now increased the discussion to include the formation of

vibrationally excited CB and the atmospheric modelling section has been extended to include discussion of the impact of YSCI.

3. We are happy that the referee finds the HCOOH yields as a function of RH interesting. Indeed, this is the major finding of this work. It should be pointed out that our results agree with previous data. We are unsure as to how we can include a discussion on anti/syn for the O_3-ethene system, as a result of symmetry there is no possibility for the formation of such isomers. Indeed, the work of Kuwata et al., does not present calculations on the ethene system, for this reason.

4. Alam et al., 2010 do not measure HCOOH, however they report that the radical yields reduce as a function of RH, i.e. the CB is reacting to form a stable species, such as HCOOH. We did not refer to the work of Tillmann et al., 2010 as it does not report on the ozonlysis of ethene, but that of alpha pinene. However Tillmann et al., do observe an increase in in the yield of pinonaldehyde as a function of RH as a result of the increased titration of the SCI. The result of Tillmann et al., would suggest the reaction of SCI with water is a ubiquitous phenomenon with far reaching implications for tropospheric chemistry.

References

Alam, M. S., Camredon, M., Rickard, A. R., Carr, T., Wyche, K. P., Hornsby, K. E., Monks, P. S., and Bloss, W. J.: Total radical yields from tropospheric ethene ozonolysis, Phys. Chem. Chem. Phys., 13, 11002-11015, 2011.

Aschmann, S. M., Arey, J., and Atkinson, R.: OH radical formation from the gas-phase reactions of O3 with methacrolein and methyl vinyl ketone, Atmos. Environ., 30, 2939 – 2943, doi:10.1016/1352-2310(96)00013-1, 1996.

Bauerle, S., and Moortgat, G. K.: Absorption cross-sections of $HOCH_2OOH$ vapor between 205 and 360 nm at 298 K, Chem. Phys. Lett., 309, 43-48, 1999.

Grosjean, D., Williams, E. L., and Grosjean, E.: Atmospheric chemistry of isoprene and of its carbonyl products, Environ. Sci. Technol., 27, 830–840, doi:10.1021/es00042a004, 1993.

Kroll, J. H., Sahay, S. R., Anderson, J. G., Demerjian, K. L., and Donahue, N. M.: Mechanism of HOx formation in the gas-phase ozone-alkene reaction. 2. Prompt versus thermal dissociation of carbonyl oxides to form OH, J. Phys. Chem. A, 105, 4446-4457, 2001a.

Kroll, J. H., Sahay, S. R., Anderson, J. G., Demerjian, K. L., and Donahue, N. M.: Mechanism of HOx formation in the gas-phase ozone-alkene reaction. 2. Prompt versus thermal dissociation of carbonyl oxides to form OH, J. Phys. Chem. A, 105, 4446-4457, 2001b.

Kuwata, K.T., Hermes, M.R., Carlson, M.J., and Zogg, C.K.: Computational Studies of the Isomerization and Hydration Reactions of Acetaldehyde Oxide and Methyl Vinyl Carbonyl Oxide, J. Phys. Chem. A. 114, 9192–9204, 2010.

Minkoff, G. J.: The Infra-Red Absorption Spectra of Organic Peroxides, Proceedings of the Royal Society of London Series a-Mathematical and Physical Sciences, 224, 176-191, 1954.

Donahue et al., Donahue, N.M., Drozd, G.T., Epstein, S.A., Presto, A.A., and Kroll, J.H., Adventures in ozoneland: down the rabbit-hole, Phys. Chem. Chem. Phys., 13, 10848-10857,2011.

Ryzhkov, A. B., and Ariya, P.A.: A theoretical study of the reactions of parent and substituted Criegee intermediates with water and the water dimer, Phys. Chem. Chem. Phys., 6, 5042-5050, 2004.

Tillmann, R., Hallquist, M., Jonsson, A. M., Kiendler-Scharr, A., Saathoff, H., Iinuma, Y., and Mentel, T. F.: Influence of relative humidity and temperature on the production of pinonaldehyde and OH radicals from the ozonolysis of alpha-pinene, Atmos. Chem. Phys., 10, 7057-7072, 2010.