

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.

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This article presents an experimental determination for the ratio k_3/k_4 , with k_3 the rate coefficient for the reaction of CH_2OO with H_2O , and k_4 the decomposition rate for CH_2OO . The result confirms the dominance of the reaction with H_2O in atmospheric condition. However, the claim that the reaction between CH_2OO and water “may dominate the production of HC(O)OH ” seems quite exaggerated, for several reasons:

- CH_2OO is produced only from the ozonolysis of terminal alkenes (e.g. Neeb, 1997) i.e. not from α -pinene. The 4.1% HCOOH yield measured by Lee et al. (2006) in the ozonolysis of α -pinene cannot be due to the $\text{CH}_2\text{OO}+\text{H}_2\text{O}$ reaction.

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Likewise, Larsen et al. (2001) presented OH-initiated oxidation experiments, not ozonolysis experiments as stated here. The high HCOOH yields reported by Larsen et al. (2001) were very probably due to secondary chemistry, given the strongly oxidative conditions in these experiments.

- The estimate of 23.6 Tg HCOOH produced in the ozonolysis of isoprene seems too high. Details should be provided regarding (1) the assumed HCOOH yield, and (2) the fraction of isoprene oxidized by O₃ in the model. Measurements put the yield of stabilized CH₂OO from isoprene between 0.16 and 0.30 (Neeb et al., 1997; Hasson et al., 2001). Similarly, details are needed for the HCOOH production estimate from MACR and MVK.
- It is assumed here that HMHP decomposes spontaneously to HCOOH. But HMHP has been commonly observed at substantial levels (up to several ppbv) in the boundary layer over isoprene-rich areas (Lee et al., 1993; Sauer et al., 2001; Valverde-Canossa et al., 2006), suggesting that decomposition is slow in atmospheric conditions. I understand that wall losses for O₃ and HCOOH were determined to be slow in this study; but does that preclude wall loss of HMHP (and subsequent conversion to HCOOH), in particular in the 70 cm long narrow PFA tube which couples the reaction chamber to the CIMS? Additional experiments could be performed using different PFA tube lengths to test the influence of such wall losses.

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