**Atmospheric
Chemistry
and Physics
Discussions**

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.

D. J.-F. Müller

jfm@aeronomie.be

I thank C. Percival for his answer to my comments. Find below further reactions to the article and to C. Percival's comments.

"(...) What is clear is that models currently underestimate formic acid in the atmosphere and we have identified a possible significant source of formic acid. (...) what we are reporting in this paper is that, using our result, ozonolysis would contribute to the global budget in the atmosphere."

The significant contribution of alkene ozonolysis to the budget of HCOOH is well known since many years. The production of formic acid from the reaction of stabilised CH_2OO

biradicals with H_2O was proposed 30 years ago (Hatakeyama et al., 1981; Atkinson and Lloyd, 1984). Formation of HCOOH from ozone+alkenes reactions has been included in many model studies (Jacob and Wofsy, 1988; von Kuhlmann et al., 2003; Ito et al., 2007; Paulot et al., 2011), although these models consistently underestimate the observed atmospheric concentrations of formic acid.

"(...) on the basis of experimental evidence by Larsen relative to Glasius et al., it seems that ozonolysis is the dominant route."

As I explained in my previous comment, the studies of Larsen et al. and Glasius et al. do not provide any evidence that ozonolysis is a dominant route for HCOOH production from terpenes, compared to OH-oxidation.

"Given that $[H_2O]$ will vary from $\sim$ 2 - 6 $\times$ 10^{17} molecule cm^{-3} the loss rate with respect to water in the atmosphere would range from $\sim$ 2 s^{-1} to 6 $\times$ 10^5 s^{-1}. Loss via unimolecular decomposition can vary from 0.3 – 250 s^{-1} (Fenske et al., 2000)."

The unimolecular decomposition rate determined by Fenske et al. (2000) applies to *stabilised* Criegee Intermediates (SCIs), not to the nascent, chemically activated Criegee Intermediates (CIs). There seems to be a recurring confusion by Leather et al. between SCIs and the "hot" CIs.

"As shown in our paper, figure 6, our results agree with 3 previous studies of the formic acid yield from ozonolysis of alkenes as a function of RH."

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 is close to 0.4. However, the interpretation of the results ignores almost completely the wealth of previous laboratory and theoretical studies of the $C_2H_4+O_3$ system (see e.g. Alam et al., 2011 and references therein; the IUPAC recommendation: http://www.iupac-kinetic.ch.cam.ac.uk/datasheets/pdf/Ox_VOC5_O3_C2H4.pdf). It appears from many studies that only a fraction (between 0.35 and 0.54) of the energy-rich CIs is colli-

sionally stabilised. The rest undergoes "prompt" unimolecular reactions at the time scale of a single collision, i.e. much faster than bimolecular reactions (e.g. Kroll et al., 2001). This questions the good agreement of the simple model represented by reactions (R2) and (R3) with the observed HCOOH yields (Fig. 7), since this model ignores the existence of prompt unimolecular reactions. An alternative model should be tested, accounting for these prompt reactions. My guess is that a stabilisation fraction of 0.54 (Alam et al., 2011) would do a reasonable job, if the ratio (k_3/k_2) is reduced by a factor of about 4.

References

Alam, M. S. et al. *Phys. Chem. Chem. Phys.* **13**, 11002—11015, 2011.

Atkinson, R. & Lloyd, A. L. *J. Phys. Chem. Ref. Data* **13**, 315–444, 1984

Fenske et al., *J. Phys. Chem. A* **104**, 9921—9932, 2000.

Hatakeyama, S. et al. *J. Phys. Chem.* **85**, 2249–2254, 1981.

Jacob, D. J. & Wofsy, S. C. *J. Geophys. Res.* **93**, 1477-1486, 1988.

Kroll, J. H. et al. *Phys. Chem. Chem. Phys.* **105**, 4446–4457, 2001.

———————————————————

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

C10877