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Atmospheric Chemistry and Physics
Discussions

Interactive comment on "A large and ubiquitous source of atmospheric formic acid" *by* D. B. Millet et al.

D. B. Millet et al.

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Thank you for the review.

The paper is well written, draws clear conclusions from their study and is certainly worth to be published in ACP. I have only a few minor comments:

Page 4546: there is a very new paper on the rate of Criegee with H2O (Chao, W.; Hsieh, J.-T.; Chang, C.-H.; Lin, J. J.-M. Direct kinetic measurement of the reaction of the simplest Criegee intermediate with water vapor. Science 2015, 347, 751-754.) which confirms that the reaction takes place with the water dimer. Even though this doesn't change any conclusion of the current paper, it would be good to include this reference in the discussion.

Thanks for pointing this out. We have added the reference as suggested.

Page 4547, line 3: you say hot formic acid might decompose to peroxyacyl radicals, that subsequently could react with HO2 to form HCOOH. I can't follow this: I would think that hot formic acid would decompose to OH and the acyl radical, and the acyl radical would under atmospheric conditions always react to HO2 and CO. Could you be more precise in this point?

Thank you for catching this! We have removed that text.

Page 4551, line 13: the absorption cross section has not been measured by Bossolasco et al, but by Faragó, E. P.; Viskolcz, B.; Schoemaecker, C.; Fittschen, C. Absorption Spectrum and Absolute Absorption Cross Sections of CH3O2 Radicals and CH3I Molecules in the Wavelength Range 7473–7497 cm–1. The Journal of Physical Chemistry A 2013, 117, 12802-12811.

We have now clarified this point as requested.

In the same paragraph at the end you say that the rate constant would be fast enough to represent an important CH3O2 sink and you cite the same three papers as for the absorption cross section: it would be more appropriate to cite: Fittschen, C.; Whalley, L. K.; Heard, D. E. The Reaction of CH3O2 Radicals with OH Radicals: A Neglected Sink for CH3O2 in the Remote Atmosphere. Environ. Sci. Technol. 2014, 118, 7700–7701.

Agreed, and done.

Page 4563, line 25: does your model contain already the new, fast rate constant for the Criegee + SO2, such as published by Welz et al? I'm not sure if MCMv3.2 has already been updated?

No, as stated we use MCMv3.2 for CH2OO + SO2, NO, NO2 and CO. As the reviewer points out, Welz et al. report a faster rate coefficient for CH2OO + SO2 than is employed by MCM3.2 (or the updated MCM3.3). We have added a refer-

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ence to Welz et al. 2012 in our statement that "If the actual rate is significantly slower than the values applied here (or the rates for competing SCI reactions are faster; e.g., Welz et al., 2012) then the role of CH2OO + H2O as a source of HCOOH would decrease."

Page 4566, discussion on the influence of CH3O2 + OH: I understand that you have removed all experimental data showing high NOx concentration before comparing with the model? However, a possible bias to the reaction CH3O2 + OH would be probably detected if the NOx dependence would be observed: the reaction of CH3O2 + OH becomes much less important with increasing NOx. So if a sizeable fraction of HCOOH would originate from CH3O2 + OH, the model should perform better at higher NOx concentrations: do you see any trend in the bias of the model with NOx concentration?

We have not attempted to remove all the high NOx concentrations, just the concentrated fresh plumes that are not resolved at the model resolution. This is a nice idea, but the challenge for this dataset is that as NOx changes, all of the other HCOOH sources presumably change as well in some fashion (due to differing precursors, chemistry, extent of photochemical aging, etc), so it would be difficult to isolate the effect of CH3O2 in this way.

Concerning the rate constant of CH3O2 + OH, did you test a lower rate constant to see if the CH3OOH results would be less degraded while still adding to the missing HCOOH budget? Recent measurements of the rate constant for C2H5O2 + OH using different precursors find a lower value of 1.2e-10 (Faragó, E. P.; Schoemaecker, C.; Viskolcz, B.; Fittschen, C. Experimental determination of the rate constant of the reaction between C2H5O2 and OH radicals. Chem. Phys. Lett. 2015, 619, 196-200.).

Indeed, we did test the impact of a reduced CH3O2 + OH rate constant (or, equivalently for the purposes of HCOOH production, a reduction in the yield of HCOOH from that reaction). This is illustrated in Fig 13 (Fig 12 of the revised version), which shows that a combination of a reduced source from CH3O2 + OH plus an

increased source from biogenic VOC can fit the observed SENEX profile. This discussed at the top of p.4568 of the ACPD paper. We did not do an explicit comparison of CH3OOH for this scenario, as it was meant to be illustrative and Figure 14 (Fig 13 in the revised version) already shows the bounding cases of k(CH3O2+OH) = 0 and k(CH3O2+OH)=2.8e-10. The results for CH3OOH shown in Fig 14 (Fig 13 in the revised version) would fall between these two profiles given a slower CH3O2+OH rate coefficient.

A very recent work on the reaction of CH3O2 + BrO (Shallcross, D. E.; Leather, K. E.; Bacak, A.; Xiao, P.; Lee, E. P. F.; Ng, M.; Mok, D. K. W.; Dyke, J. M.; Hossaini, R.; Chipperfield, M. P.et al. The Reaction between CH3O2 and BrO Radicals: a New Source of Upper Troposphere Lower Stratosphere Hydroxyl Radicals. The Journal of Physical Chemistry A 2015, doi:10.1021/jp5108203.) finds the Criegee intermediate to be the major reaction product. You could cite this work as an analogous reaction to CH3O2 + OH, nex to the reaction CH3O2 + Cl.

Done.

Interactive comment on Atmos. Chem. Phys. Discuss., 15, 4537, 2015.