Review for: acp-2013-922

Online measurements of water-soluble organic acids in the gas and aerosol phase from the photooxidation of 1,3,5-trimethylbenzene

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This manuscript reports identification and quantification of organic acids from the photooxidation of 1,3,5-TMB (OH produced by ozone photolysis) at initially-high NO and NO_2 conditions at RH ~ 50%. Organic acids were collected in the gas phase by a wet effluent diffusion denuder and in the aerosol phase by a wet filter. Quantification of common organic acids was performed with the aid of authentic standards using ion chromatography (IC). A high-resolution mass spectrometer (Orbitrap) was used for identification of molecular formulas. For organic acids identified only by molecular formula, surrogate calibration curves were used. TMB was quantified using PTR-MS. The work contains results that are relevant to the gas- and aerosol-phase composition in urban atmospheres. There are several interesting observations in the paper that may benefit from additional development. Thus, this work is suitable for publication in ACP, after addressing the comments below:

General comments:

The photooxidation transitions from high NOx/ low ozone to low NOx/ high ozone, and thus, the sources of gas- and aerosol-phase organic acids is difficult to pinpoint. Does the chemical regime change affect the composition in the gas phase and aerosol phase at all? In particular, it would be useful to discuss explicitly the reasons why SOA formation occurs when NO is low. It is implied that when NO drops, O_3 increases and the reaction can proceed due to the production of OH. In that way, is the composition of the SOA produced only relevant to low-NO/high ozone conditions? In Figure 4b, it seems that for the 1200 ppbv TMB experiments, [OH] is constant at ~ 5×10^5 molec cm^{-3}, even when TMB is not reacting away (hours 0 – 2). As OH was produced by O_3 and its mixing ratio calculated from TMB decay, why is [OH] not lower when the TMB decay and $[O_3]$ was negligible?

As the first-generation photooxidation products of TMB contain abundant ring-opening alkenes according to MCM (Metzger, ACP, 2008), high ozone toward the middle to end of the photooxidation might play a significant role in the organic acid formation. The authors have acknowledged this briefly in the paper, but it would be useful to add a discussion about how ozonolysis vs. OH oxidation (high and low-NO) contribute to the results.

The role of particle liquid water should be explored in more detail in this work because it is important to the understanding of gas/particle partitioning and ozonolysis in formation of aerosol-phase organic acids. See specific comment #7 and #12. Can the authors estimate the particle liquid water for each experiment (will there be any for organic-only particles at RH ~ 50 %?), and address if the addition of SO_2 will change the particle liquid water or particle pH?

Specific comments:

1. Page 986, lines 12 – 13 (and page 997, 1000): It's not clear to me how the 6 – 14% range is derived. At hour 4, the 1200 ppbv TMB experiment yielded 20% organic acid and the 600 ppbv TMB experiment yielded roughly 10%. At hour 6, the 1200 ppbv experiment yielded 6-7% and the 600 ppbv experiment yielded ~ 10%. Are the authors expecting a constant yield, and taking an average? Does the different time-dependence of the acid concentration and the absolute yields indicate possible differences caused by precursor concentration? A known mechanistic difference is the prevalence of RO_2 + RO_2 radical chemistry at high precursor concentration, which would be dependent on concentration squared. I don't believe the authors have enough evidence in the data set shown to conclude that "organic acid fraction present in the aerosol phase does not strongly depend on the precursor concentration."

2. Page 987, lines 11-12: I think this is a misprint – the authors could not have meant that the hot Criegee intermediate can be stabilized by the HO_2 radical to anything more than a very negligible fraction. Certainly they won't find support of this statement in the current citation of Maldronich et al (1990). Rather, Maldronich et al cites Calvert et al (1978), who describe a unimolecular source of organic acids, which is by the isomerization of Criegee intermediates (specifically those in the *anti* conformation). Stabilization of hot Criegees is facilitated by bath gasses and water vapor in the atmosphere. These stabilized Criegees can react with water vapor to form organic acids (see, for example Horie et al, JGR 1994, who first describe the reaction). The bimolecular reaction might be important in this work (for Criegees produced from O_3+ ring-opening oxidation products of TMB from the middle to end of the reaction) because there is something like 1500 ppmv of water vapor in the reaction. Both the unimolecular and bimolecular reactions should be noted here, including the citations inserted.

3. Page 987, lines 16 – 21: This implies that all online detection methods of organic acids either have high limits-of-detection or extensive fragmentation of the molecules, which is misleading. The authors only cite PTRMS for support; when there are sensitive (LOD ~ 1 pptv) and fast (up to 10 hz) CIMS techniques that can detect organic acids without fragmentation and with mass resolution typical of a time-of-flight detector. For example: CIMS techniques using Acetate anion (Veres et al, Int J. Mass Spectrom 2008), Iodide anion (Le Breton, Atmos. Meas. Tech., 2012), and CF_3O^- anion (Paulot et al, ACP 2009) as reagents can all detect various organic acids in-situ. These citations should be included for a more thorough and balanced representation.

4. Page 988, lines 24 – 26: It should be explicitly stated that PTR-MS was used to measure TMB in this work. Also, the calibration and error estimation for TMB should be discussed (was it using the standard PTR rate coefficient, in which case error is a factor of two, or calibrated directly assuming quantitative transfer of TMB, in which case the error is the uncertainty in the transfer process?)

5. Page 996, lines 22 – 24: The authors should note that, if the relatively high Welz et al (2012) rate coefficient for stabilized Criegee + SO_2 measured at low pressure (*k* @ 4 Torr ~ 4×10^{-11} cm^3 $molec^{-1}$ s^{-1}) is robust and can be extrapolated to atmospheric pressure,

then 2 ppb of SO_2 can be competitive with the water vapor found at RH ~ 50% at T ~ 20 degC only if the rate of stabilized Criegee + H_2O reaction is at the low end of the measurement range found in literature (10^{-15} – 10^{-19} cm^3 $molec^{-1}$ s^{-1}). The uncertainties in these rates are still very high (several orders of magnitude difference depending on the study), and they are the subject of ongoing investigations.

6. Page 996, lines 24 – 26: Why would ozonolysis just impact lactic acid formation, but not the formation of other carboxylic acids (specifically formic)? Is there a mechanism that the authors can suggest to justify this claim?

7. Page 997, lines 5-7: The effect of particle-phase H_2SO_4 on the partitioning of organic acid should be discussed in more detail. On the one hand, the lower particle pH will suppress the dissociation of organic acids, shifting the equilibrium toward the gas-phase. However, more H_2SO_4 in the particle increases the particle liquid water due to the large hygroscopicity of H_2SO_4, which may increase the partitioning of organic acids (Liu et al, JGR 2012). It is crucial, then, to know the quantity of particle liquid water and the activity of $[H^+]$ in the particle water in order to speculate on the effects of acid on the partitioning. Can the authors calculate how the pH of the particle will be impacted by adding 2 ppb of SO_2, knowing the effective Henry's equilibrium of SO_2 (which can be found on the NIST website)?

8. Page 997, lines 17-21: How do the authors know the shape of an unidentified compound?

9. Page 998, line 9: Where does the nitric acid come from? And is it only the dominant inorganic species in aerosols without SO_2? If AMS data is available, can the authors report the particle sulfate concentration from the addition of SO_2?

10. Page 998, lines 15 – 17: The effect of SO_2 on aerosol-phase glycolic acid appears to be within the error of the measurement.

11. Page 998 – lines 20 – 24: For experiments with SO_2, can pH ~ 4 still be assumed when calculating the partitioning coefficient?

12. Page 999, lines 11 – 16: For this experiment, 1200 ppbv TMB at 50% RH, there was no added SO_2. The authors state that TMB SOA is only weakly hygroscopic (Page 992, lines 11 – 12, citing Duplissy et al 2011). Therefore, for organic-only TMB aerosol, was there any liquid water for the acetic acid that was present in the experiment or the added acetic acid to partition?

13. Page 999, lines 14-15: What is the Henry's law coefficient that was used (and the citation) and what was the assumed liquid water content that would yield 170 – 2100 ng m^{-3} expected acetic acid in the condensed phase?

14. Page 1000, lines 5 – 8: It should be noted that the reactive uptake and oligomerization reaction mechanisms in aldehydes are different than that for organic acids (e.g., geminal diol formation and nucleophilic addition in aldehydes vs. weak acid dissociation in

organic acids; and hemiacetal formation in aldehydes and esterification if there is an alcohol group present in organic acids). Thus, I'm not sure how the results of Healy et al (2008) can be relevant here.

15. Figure legends (and text) – Can I suggest the authors label the experiments with the mean OH concentration of the experiment for easier interpretation of the figures, as the main differences in NOx/O3 and particle mass fraction are due to OH concentration, not added SO_2. For example, 600 ppbv TMB + SO_2 (5 x 10^6 OH) vs. 600 ppbv TMB (4 x 10^5 OH).

Typos

Page 997, lines 2-4: I believe it should be Figure 8 b and d (not 8c) that shows the SO_2 results.

References

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