

Interactive
Comment

***Interactive comment on* “Online measurements of water-soluble organic acids in the gas and aerosol phase from the photooxidation of 1,3,5-trimethylbenzene” by A. P. Praplan et al.**

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General comments:

Organic acids are an important class of compounds identified in the chemical analysis of atmospheric secondary organic aerosol (SOA) particles and have potential impacts on climate, human health, and visibility. The authors report the results of a laboratory study of organic acid formation during the photo-oxidation of 1,3,5-trimethylbenzene (TMB). TMB is a typical precursor of SOA particles in urban air. A series of photo-oxidation experiments were conducted using an environmental chamber. The photo-

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oxidation of TMB was investigated under high-NO_x conditions. Gaseous and particulate organic acid products were sampled using a wet effluent diffusion denuder (WEDD) and an aerosol collector (AC), respectively. Gaseous and particulate organic acids were analyzed by an online ion chromatography (IC) instrument coupled with a mass spectrometer (MS). The authors identified twelve organic acids in the gas and particle phases. They measured the gaseous and particulate concentrations of twelve acids as a function of time. They also investigated effects of the initial TMB level, SO₂ addition, and gaseous acetic acid injection during photo-oxidation. The particulate organic acid levels were much higher than those expected based on a gas/particle absorptive partitioning model. No apparent increase in particulate acetic acid concentration was observed after a large amount of gaseous acetic acid was injected. The authors suggest that the presence of small acids in the particle phase is not due to partitioning effects, but they are mainly produced by the hydrolysis of ester oligomers during sampling or in the particle phase. This result will provide new insight into the formation processes of small organic acids detected by the chemical analysis of SOA particles. The topic discussed in this report fits the scope of Atmospheric Chemistry and Physics. This paper will be publishable after appropriate revisions are made, taking into account the following comments.

Specific comments:

- 1) P989, L1-16: Did the authors correct or evaluate the errors resulting from the collection efficiencies of the WEDD and AC instruments?
- 2) P989, L17-26: Did the authors use any internal standards to monitor the sensitivity variation of the IC/MS instrument? It would be useful to discuss the error resulting from such sensitivity variation.
- 3) P992, L1-2: What is “a theoretical range”? It would be useful to specify whether this “theoretical range” is the uncertainty in the saturation vapor pressure predicted by the structure-based method or a vapor pressure range for the acidic and neutral particles.

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The authors do not discuss the uncertainties in the vapor pressures predicted by the structure-based method. Does one obtain the same conclusion in section 3.4 if these uncertainties are taken into account?

4) P999, L11-21: When a large amount of acetic acid was injected, the oligomerization of acetic acid and the absorption of acetic acid by existing particles were both negligible. Can the author discuss why such oligomerization did not occur?

5) Section 3.4 and conclusions: The authors suggest that the particulate carboxylic acids detected are mainly produced by the hydrolysis of oligoesters during sampling or in the particle phase. Are the oligoesters produced by particle-phase oligomerization between organic acids and alcohols (Surratt et al., 2010)? Are the organic acid monomers produced by gas phase reactions and then absorbed by particles? Can organic acid formation in the aqueous phase play any role under present RH conditions? It would be useful to discuss the reaction mechanisms of carboxylic acid formation and the oligomerization of carboxylic acids during the oxidation of TMB.

Other comments:

1) P986, Abstract: It might be useful to describe that experiments were conducted in the presence of NO_x.

2) P987, L6-15: Surratt et al. (2010) have recently proposed that organic acids are formed by the decomposition of peroxyacyl nitrates (PANs). It might be useful to add a description of organic acid formation by the decomposition of PANs here.

3) P988, L10-11: What cut-off filters were used for the xenon lamps?

4) P988, L21-24: The names of the suppliers of the ozone monitor, NO_x monitor, CPC, and SMPS are missing.

5) P989, L17-26: The explanations of the eluent flow rate and the source of the OH⁻ anions are missing.

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6) P991, L22-23: How did the authors evaluate the mean MW of the absorbing material?

7) P993, L3-4: The authors assume that TMB reacts only with OH radicals. On the other hand, in the introduction, the authors assert that aromatic compounds are oxidized by OH or NO₃ radicals. Both descriptions are acceptable and correct, but some readers may be confused by these two sentences. It would be useful to note that aromatic “hydrocarbons” are predominantly oxidized by OH radicals under atmospheric conditions.

8) P994, L13-14: Can the authors provide the NO₂ photolysis rates for the black lights and the xenon lamps?

9) P994, L16-17: What is compared with the aerosol mass measured using black light in the presence of SO₂?

10) P995, L10-11: As for chemical structures proposed by Sato et al. (2012), they state that some isomers are likely although only one isomer is shown for simplicity. Please see the table footnotes in their paper.

11) P995, L11-14: Another explanation is also possible: compounds separated by the LC instrument used by Sato et al. (2012) may not be separated by the present IC/MS instrument.

12) P996, L9: The authors identified M234 product as dicarboxylic acid. The retention time for the IC might depend not only on the number of carboxylic groups but also on the chemical structure. It would be useful to explain how the authors identified chromatographic peaks as mono- or dicarboxylic acids.

13) P996, L14-15: Sato et al. (2007) suggested that a similar hydrolysis process occurred during the pretreatments of off-line toluene SOA samples. Please cite this result.

14) P996, L18: The authors use “butyric acid” here although they use “butanoic acid” in other instances in this paper. Please use a single terminology throughout the text.

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15) P996, L24-26: What Criegee radical is the precursor of lactic acid? What reactions result in the formation of the precursor Criegee radical?

16) P997, L12-16: The present IC/MS instrument might not have sufficient sensitivities for the two peaks measured by Sato et al. (2012). Furthermore, the present IC/MS procedure might not separate the three peaks of the M234 product. If these possibilities are taken into account, is the same conclusion obtained?

17) P998, L9: The authors identified AMS NO₃ signals as nitric acid. However, nitroaromatic compounds and organic nitrates are also potential sources of these NO₃ signals (Liu et al., 2012; Sato et al., 2012). Nitroaromatic compounds and organic nitrates are neutral species and would not affect the acidity of the SOA particles.

References:

Liu, S., Shilling, J. E., Song, C., Hiranuma, N., Zaveri, R.A., Russell, L.M.: Hydrolysis of organonitrate functional groups in aerosol particles, *Aerosol Sci. Tech.*, 46, 1359-1369, doi: 10.1080/02786826.2012.716175, 2012.

Sato, K., Hatakeyama, S., Imamura, T.: Secondary organic aerosol formation during the photo-oxidation of toluene: NO_x dependence of chemical composition, *J. Phys. Chem. A*, 111, 9796-9808, doi: 10.1021/jp071419f, 2007.

Surratt, J.D., Chan, A.W.H., Eddingsaas, N. C., Chan, M.N., Loza, C.L., Kwan, A.J., Hersey, S.P., Flagan, R.C., Wennberg, P.O., Seinfeld, J.H.: Reactive intermediates revealed in secondary organic aerosol formation from isoprene, *Proc. Natl. Acad. Sci. USA*, 107, 6640-6645, doi: 10.1073/pnas.0911114107, 2010.

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