

Answers to referees for “Online measurements of water-soluble organic acids in the gas and aerosol phase from the photooxidation of 1,3,5-trimethylbenzene” (acp-2013-922)

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The authors would like to thank K. Sato and the anonymous reviewers and for their helpful and thoughtful comments and suggestions. Each specific point is addressed below. Reviewer comments are in italics and our responses are in plain text.

K. Sato (Referee)

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-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?

Fisseha et al. (2004) estimated the collection efficiencies for the WEDD and AC. Formic acid and acetic acid collection efficiencies in the WEDD were 75% and 85% at a sampling flow of 4l/min. For the AC, (mass) collection efficiency was larger than 95% for ammonium sulphate particles ($D_p=10 - 220$ nm). In the revised manuscript, gas phase concentrations have been corrected assuming an average 80% collection efficiency.

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.

No internal standard was used to monitor sensitivity variation. However, liquid flows through the

WEDD and the AC were regularly controlled to ensure proper operation of the devices. Reproducibility of experiments was good in general, but only representative experiments have been included in our manuscript. Typically, the agreement from experiment to experiment is within 30%.

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. 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?*

Three different structure-based estimators for vapour pressure are available from the E-AIM model (http://www.aim.env.uea.ac.uk/aim/ddbst/pcalc_main.php), based on the *Dortmund Data Bank* (DDB, provided by DDBST GmbH, Germany). Also EVAPORATION (Compennolle et al. 2011) provides estimates for vapour pressures of organic compounds. As “theoretical” was not an appropriate word, we have rewritten this paragraph. We additionally estimated $K_{p,eff}$ assuming pH values of 2 and 4. From all the estimated K_p and $K_{p,eff}$ values, the minimum and the maximum were used to define the “expected range” of K_p in Fig. 9, as an estimate of the uncertainties. This is now better explained in the revised manuscript main text and caption of Fig. 9.

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?*

The idea of the experiment was to check if there is unexpected partitioning, reactive uptake or oligomerisation. None of these processes occurs. Actually we do not expect partitioning based on the volatility of acetic acid. We are not aware of a mechanism that acetic acid must oligomerise. The mechanism of oligomerisation is still fairly unclear. Some experiments have shown that esterification can take place. Our results show that either it does not occur or it is not reversible.

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., 2009)? 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.*

We agree with the referee that oligomerisation processes probably leading to detection of carboxylate ions in our instrument must be discussed in more detail (see comments from Anonymous Referee #3). The authors assume that organic acids are products of gas phase reactions. The liquid water content of the particle remain small under the present RH conditions, so that the authors expect aqueous oxidation to play a minor role. (See further discussion of later referees' comments.)

Other comments:

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

The abstract now contains “in the presence of NO_x ”.

2) P987, L6-15: *Surratt et al. (2009) 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.*

The reference suggested has been included in the organic acid formation mechanisms. The whole

paragraph has been edited following a comment from Anonymous Referee #2 pointing to a misquotation of a cited manuscript.

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

We use a borosilicate glass filter ("selected white floatglass", SWF, Praezisions Glas & Optik GmbH, Germany) with a transmission of 50% at 310 nm. More details are described in Paulsen *et al.* (2005), as stated at the beginning of the smog chamber description.

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

The name of suppliers and more details about the instrumentation have been inserted in the revised manuscript.

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

The flow rate used was 0.25 ml/min and OH⁻ anions were generated from KOH by an Eluent Generator (EG40, Dionex) from a KOH solution (Eluent Generator Cartridge). This information is now included in the revised manuscript, also addressing the comment from Anonymous Referee #3.

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

The value of 130 g/mol has been estimated from an average between highly oxidised species and water as absorbing mass.

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.*

We thank the referee to point out this inconsistency in our text. We included an additional sentence in the manuscript to explain that NO₃ radical is photolysed under the present experimental conditions and do not contribute to TMB oxidation: "Note that NO₃ radicals do not play a role in TMB photooxidation under these experimental conditions; it is rapidly photolysed to NO or NO₂."

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

The NO₂ photolysis rate ca. 10⁻³ s⁻¹ for the xenon lamps and ca. 1.5 · 10⁻² s⁻¹ with additional black lights. These values are included in the revised manuscript.

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

We removed the comparison from this sentence in the revised manuscript as we do not present data for 600ppb of TMB photooxidation in the presence of SO₂ using only the Xenon arc lamps. The statements about larger TMB reacted and reduction of wall losses remains correct, though.

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.*

The authors are aware that the structural isomers shown in Table 2 of Sato *et al.* (2012) are not unique. The authors of the present manuscript meant that Sato *et al.* were able to identify unique elemental composition, compared to the results in this manuscript where even the elemental

composition could not be identified unambiguously. Because the use of the term “chemical composition” was misleading, it is now replaced by “elemental composition” and this part of the paragraph has been rewritten for more clarity.

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.

It is possible that compounds with same molar masses could not be separated by ion chromatography in our study. It is now clearly mentioned in the revised manuscript.

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.

The separation between mono- and dicarboxylic acids is solely based on the retention time of corresponding peaks. Compounds with retention time shorter than 17 min are monocarboxylic acids, while compounds with longer retention time have been attributed to dicarboxylic acids. The discussed unknown compound with molar mass 86 must be a monocarboxylic acid, as the lightest possible dicarboxylic acid (oxalic acid) has a molar mass of 90. One compound with molar mass had a very close retention time and was tentatively attributed to a dicarboxylic acid (Table 1). Therefore, with a retention time longer than 18 minutes, the compound with molar mass 234 has to be a dicarboxylic acid.

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.

We thank the reviewer to bring this publication to our attention. It has been now included in the revised manuscript.

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.

The authors thank the referee for identifying this inconsistency. The IUPAC name “butanoic acid” is used consistently in the revised manuscript.

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

The question is how SO₂ can directly interfere with the degradation mechanism of TMB. To our knowledge is the reaction with a Criegee radical the only possible pathway. This is a hypothesis and cannot be proven from these experiments. It is known that unsaturated degradation products are formed like 2-methyl-4-oxo-2-pentenal which can undergo ozonolysis forming Criegee radicals. A mechanism forming lactic acid is possible with this compound but highly speculative. The reaction between SO₂ and the Criegee radical can only be important if the competitive reaction with water is very slow (see also specific comment 5 by Anonymous Referee #2). This is now discussed.

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?

It is true that the comparison of our results with the ones from Sato *et al.* (2012) was not properly addressed. The discussion has been revised and we conclude that at least one of the peaks detected by Sato *et al.* (2012) should be a dicarboxylic acid, according to our finding.

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.*

The authors agree that organic nitrates can potentially be attributed to AMS NO₃ signal. However, not only based on AMS measurement, but also on IC/MS results, it is possible to say that NO₃⁻ and HSO₄⁻ are the main aerosol species (See also answer to previous comments). However, the inorganic fraction of the aerosol remain mainly below 5%. This information is better integrated in the revised manuscript.

Anonymous Referee #2

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 NO₂ 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 NO_x/low ozone to low NO_x/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, O₃ 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 x 10⁵ molec cm⁻³, even when TMB is not reacting away (hours 0 – 2). As OH was produced by O₃ and its mixing ratio calculated from TMB decay, why is [OH] not lower when the TMB decay and [O₃] 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 SO₂ will change the particle liquid water or particle pH?

We thank the referee for the detailed suggestions to improve the quality of the manuscript.

Regarding the low-NO/high ozone conditions, we now discuss indirectly the influence of organic acids produced by ozonolysis due to the lower concentration with the same precursor level in the presence of SO₂ in certain cases (See answer to specific comment 6). This mechanism is only an hypothesis, but could under certain conditions play a role. We also elaborate the discussion about ozonolysis of primary oxidation products.

In Fig. 4 (b), the time axis was not set properly. It has been corrected in the revised manuscript. [OH] is smaller at the beginning of the experiment (ca. 10^5 cm^{-3}) and increases as the slope of TMB reacted is steeper.

From Duplissy *et al.* (2011), the growth factor of TMB SOA is approximately 1.15 after 5 hours of oxidation, which represents less than 0.2% of water (based on volume). Our IC/MS system measures bisulphate and nitrate as well and there were no large difference in their respective concentrations for the experiments with and without SO₂: nitrate mass fraction was always smaller than 4% and bisulphate was detected only in one of the experiment (LOD: 17 ng/m³) with a mass fraction below 0.1%. Therefore, we expect that the addition of SO₂ to have a marginal influence on liquid water content, which does not exceed a few percent (Kleindienst *et al.*, 1999) and particle pH. (See also answers to specific comments 7 and 12.) The main difference is the earlier formation of aerosol particles in the presence of SO₂, reducing early oxidation products losses to surfaces. Consequently, the revised manuscript clarify this and include a statement explaining that SO₂ addition affects the gas phase reactions more than the particle phase reactions.

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 RO₂ + RO₂ 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."*

Our statement about the independence of acid concentration on the precursor concentration is misleading. We meant that it is in the range of 6–20% independent of the oxidation duration for our two precursor concentrations. We agree with the reviewer, that it depends on reaction time, precursor concentration and NO_x level. The sentence was revised to: "Figure 8 (b) and (d) show a drop of the acid fraction of the main acids below 5% if SO₂ is present, while its lower limit lies between 6 and 20% in the absence of SO₂ (Fig. 8 (a) and (c))."

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 HO₂ 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 O₃ + 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.*

Our description of the stabilized Criegee intermediates' fate was indeed incorrect and has been edited in the revised manuscript, taking into account the references suggested by the referees (see comment from Anonymous Referee #3 as well). The discussion on organic acid formation also includes PANs decomposition (see other comment 5 from K. Sato).

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 CF₃O⁻ 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.

This paragraph has been edited in a more balanced way, also to take a comment from Anonymous Referee #3 into consideration.

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?)

It is now explicitly stated that the PTR-MS was used to measure TMB and was calibrated with calibration standard containing TMB.

5. Page 996, lines 22 – 24: The authors should note that, if the relatively high Welz et al (2012) rate coefficient for stabilized Criegee + SO₂ measured at low pressure ($k @ 4 \text{ Torr} \sim 4 \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$) is robust and can be extrapolated to atmospheric pressure, then 2 ppb of SO₂ can be competitive with the water vapor found at RH ~ 50% at T ~ 20 degC only if the rate of stabilized Criegee + H₂O reaction is at the low end of the measurement range found in literature ($10^{-15} - 10^{-19} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$). 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.

We agree with the reviewer that the suggested reaction cannot compete with the reaction between stabilized Criegee and water if the reaction rates are in the upper range reported in the literature. Mauldin III et al. (2012) reports also relatively high values for stabilized Criegee reaction with SO₂ (roughly one order of magnitude lower than the low pressure rate of Welz et al. (2012)). Because of the large uncertainties, we elaborate this discussion in the revised manuscript, which contains the following sentences after discussing the point of the reviewer's next comment: "However, SO₂ would be able to compete with water vapour only if the reaction rate between Criegee intermediates and water vapour is at the low end of the measurement range found in literature ($10^{-19} - 10^{-15} \text{ cm}^3 \text{ s}^{-1}$, Fenske et al. (2000), Welz et al. (2012)), due to the orders of magnitude different concentrations of SO₂ and water ($5 \times 10^{10} \text{ cm}^{-3}$ and $3 \times 10^{17} \text{ cm}^{-3}$ respectively). Due to the large uncertainties of these reaction rates, it is not possible to totally neglect this reaction path."

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?

It is not only lactic acid which is affected by the presence of SO₂. We also show it for M234 and acetic acid. It could be explained by the fact that these acids are formed via ozonolysis of TMB oxidation products, while the other ones are formed via another mechanism. (See also other comment 15 by K. Sato.) This is discussed in more detailed in the revised manuscript: "For lactic acid, a marked difference is seen comparing the 1200 ppbv TMB experiments. The presence of SO₂ decreases its concentration by roughly a factor 3. A similar effect is seen for acetic acid and M234. Recent studies show that SO₂ reacts much faster with Criegee radicals than previously reported (Welz et al., 2012; Boy et al., 2012; Mauldin III et al., 2012).

The differences in the experiments with and without SO₂ could be explained by reaction of a precursor Criegee radical with that species, hindering the formation of these acid. This is an indication that these acids would form via ozonolysis of primary oxidation products of TMB, while other acids are generated from TMB oxidation by OH.”

7. Page 997, lines 5-7: *The effect of particle-phase H₂SO₄ 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 H₂SO₄ in the particle increases the particle liquid water due to the large hygroscopicity of H₂SO₄, 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 SO₂, knowing the effective Henry's equilibrium of SO₂ (which can be found on the NIST website)?*

Partitioning of SO₂ is the first step to influence pH, but the particle phase oxidation to sulphuric acid also need to be considered. However, based on IC/MS nitrate and sulphate measurement in the gas phase, no large difference could be seen between the experiments with and without SO₂. The NO₃⁻ normalised concentration is lower than 4% and the HSO₄⁻ concentration is lower than 0.1%, when it has been detected. (Limits of detection for HSO₄⁻ range from 2.8 to 17 ng/m³, depending on the experiment. See other answers to comments as well.) This is unlikely to change the water content (a few percent of aerosol mass, Kleindienst et al. (1999)) and the pH dramatically. Therefore, our manuscript suggests now that SO₂ influences gas phase chemistry, rather than particle phase chemistry (pH and liquid water content) and do not assume that particle pH plays a major role.

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

This paragraph has been completely edited following comment from all referees and the new formulation should clarify the reasoning. For the unknown compound with the molar mass 86, only a limited number of monocarboxylic acids are possible. By elimination (three acids were available as standard, but none did have the same RT as the unknown compound), we deduced that the unidentified compound could be *cis*-2-butenoic acid. The final remark about the shape of this compound is done by comparison with *trans*-2-butenoic acid, which is expected to be more compact due to the configuration of the double-bond.

9. Page 998, line 9: *Where does the nitric acid come from? And is it only the dominant inorganic species in aerosols without SO₂? If AMS data is available, can the authors report the particle sulfate concentration from the addition of SO₂?*

Nitric acid is formed by oxidation of NO₂ by an OH radical and is indeed the dominant inorganic species in aerosols in the absence of sulphuric acid. However, its concentration remain fairly small. Unfortunately, no AMS data is available for the experiments on April 2011. Nevertheless, from IC/MS measurements, the particle sulphate concentration remain small upon SO₂ addition as no signal is observed with IC/MS, whose limit of detection is ca. 17ng/m³. (See answer to comment 7.)

10. Page 998, lines 15 – 17: *The effect of SO₂ on aerosol-phase glycolic acid appears to be within the error of the measurement.*

Our statement refers to K_p values. Even if the aerosol phase glycolic acid concentration are not very different, the gas phase concentration is slightly higher in the absence of SO₂.

11. Page 998 – lines 20 – 24: *For experiments with SO₂, can pH ~ 4 still be assumed when calculating the partitioning coefficient?*

Following the other comment 3 by K. Sato, we rewrote the explanations about the estimations of K_p and $K_{p,eff}$ values. In Figure 9, the lower limit of the estimated range is based on the lowest estimated K_p value ($K_a \ll [H^+]$, i.e. very acidic particles), while the higher limit uses $K_{p,eff}$ with a pH~4. If the presence of SO₂ and the production of sulphuric acid decreases the pH of the aerosol particles (which is likely not the case), $K_{p,eff}$ will still be in the plotted range, getting closer to the lower limit.

12. Page 999, lines 11 – 16: For this experiment, 1200 ppbv TMB at 50% RH, there was no added SO₂. 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?

We agree with the referee that the amount of water is too low in our experiments to use Henry's law. Even if acetic acid can also partition in an organic-only phase, its saturation vapour pressure is so high (ca. 1543 Pa or 1.5% mixing ratio), that was not reach with 18mg/m³ (ca. 7ppmv). It is also expected that no increase in the aerosol phase is observed.

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?

Henry's law coefficients from Sander (1999) were used. The range comes from the highest and lowest estimates found in this compilation. We assumed a liquid water content of 1, which is a “best-case” hypothesis therefore we wrote “(assuming that the aerosol would take up acetic acid as water would)”. However, we expect the liquid water content to remain fairly small in our experiments. Therefore, the authors postulate that the partitioning of organic compounds with larger molar masses according to their smaller saturation vapour pressures (no enhanced uptake) and their subsequent hydrolysis (in the case of ester or anhydride functional groups, for instance) explains best their observations.

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.

We agree with the referee that the reactive uptake reactions of aldehydes and organic acids are different. We did not mean that they are similar, but that in both cases, reactive uptake takes place and not only partitioning based on volatility. We altered slightly our sentence to make this clearer.

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 SO₂. For example, 600 ppbv TMB + SO₂ (5×10^6 OH) vs. 600 ppbv TMB (4×10^5 OH).

The referee suggestion has been implemented in the figure legends and the main text of the revised manuscript and the authors agrees that it eases interpretation of figures.

Typos

Page 997, lines 2-4: I believe it should be Figure 8 b and d (not 8c) that shows the SO₂ results.

Correct. This typo has been corrected in the revised manuscript.

Anonymous Referee #3

The manuscript of Praplan et al. reports results from investigation of water-soluble organic acids

from photooxidation of 1,3,5-trimethylbenzene (TMB) using an online system for ion chromatographic separation before mass spectrometric identification.

The study is interesting since the authors have developed an online IC-MS method for analysis of organic acids based on a previous work from the same group published a decade ago (Fisseha et al., 2004). Unfortunately, the method is hampered by high detection limits and uncertainty compared to the actual concentrations for some types of samples (typically particle samples). Generally the background, methods and results are well presented, but I have raised a number of specific issues below, which should be adequately answered before publication.

Abstract: There is no need to define the abbreviation PSI here, since it is not used further in the abstract. The last sentence of the abstract should be a bit further explained in order to be meaningful.

The PSI abbreviation has been removed from the abstract and the last sentence has been edited in order to clarify its meaning.

Page 986 Line 25. At least one reference is needed to support this.

Kroll and Seinfeld (2008) as well as Hallquist *et al.* (2009) are cited in the revised manuscript to support this statement.

Page 987: References are needed in lines 2 (... many different compounds) and line 5.

We now cite Kanakidou *et al.* (2005) and Williams *et al.* (2007) on line 2 and Saxena and Hildemann (1996) on line 5.

line 16-: Are online methods not prone to artefacts? Later in the discussion of the present manuscript, it seems that online methods may also have such problems.

The formulation of this paragraph was imprecise and partly incorrect (see comment from Anonymous Referee #2). Therefore it was rewritten taking into account available CIMS instruments and the fact that online methods, such as PTR-MS, can also show artefacts.

line 22: "the method ... allows selective collection of organic acids". I assume the authors mean water-soluble species, not just organic acids.

It is true that all water-soluble species will be collected, but on the chromatographic column, only organic compounds with at least one carboxylic acid functional group as well as a few inorganic anions (nitrite, nitrate, and sulphate) will be separated and eventually detected. The original sentence was rewritten in order to clarify it: "The ion chromatography (IC) method presented here allows water soluble organic acids (as well as nitrite, nitrate and sulphate) to be separated prior to detection."

Page 989 line 20: "hydroxy anion" should be changed to "hydroxide anion". What is the counterion (cation) in the eluent? The settings of ESI-MS should be clearly stated.

The revised manuscript uses "hydroxide anion" and includes more details regarding eluent generation. (See also answer to comment 5 from K. Sato.) The counter ion is potassium (K⁺).

The capillary voltage of the ESI-MS was set to -1.5 kV. This information has been included as well in the manuscript.

Page 991: line 7-9: Please provide more details on the sampling and extraction method.

The formed secondary organic aerosol were collected on Teflon filters when the maximum aerosol mass was reached in the chamber. The filters were extracted with water and this solution has been directly injected via a capillary and electrospray to the high-resolution mass spectrometer. This is now mentioned in the revised manuscript.

line 21: It seems that "aerosol and gas phase" should read "gas phase and aerosol".

No. The authors use the definitions from the original paper from Pankow (1994), where A_i represents the gaseous concentration and F_i the aerosol (or "particulate-associated") concentration.

Page 994: Line 3: How can the particles formed be bigger? I assume you mean that they grow to larger aerosol diameters.

Indeed, our statement was referring to the final particle diameter. This sentence has been rewritten in the revised manuscript.

line 13: Please add that the black lights were additional sources of light.

This clarification has been added to the manuscript.

line 21: What do you mean by "at least one chromatographic peak was identified of twenty-five masses.."?

Because we use mass spectrometry coupled to ion chromatography, we generate a chromatogram for each mass to charge ratio measured, also called "mass chromatogram". We mean that for twenty-five of these chromatograms, at least one peak has been identified. To make it clearer, this sentence has been modified in the revised manuscript: "Twenty-five mass chromatograms showed one or more peak. The corresponding masses are listed in Table 1 and a chemical formula could be attributed to twelve of them with the help of the high resolution MS data."

Line 25: unambiguous identification - did you have authentic standards for all compounds? Please also state in the experimental section, for which compounds you had authentic standards for quantification?

Yes, unambiguous identification is based on authentic standards. The list of these compounds is now included in the experimental section of the manuscript.

Page 995: Line 13: What were your detection limits?

Because detection limits expressed in ng/m^3 depends on the sampling flows and varies from experiment to experiment, we decided not to include detection limits in our manuscript. Additionally, calibration curves were derived from direct injection of $25\mu\text{l}$ of aqueous solutions. Therefore, the detection limits and converted signals units were expressed in ng and the gas phase and aerosol concentration expressed in ng/m^3 , taking the sampling flow into consideration. The typical range for organic acids for the WEDD and the AC devices were ranging from 0.12 to $5.1 \text{ ng}/\text{m}^3$. (For nitrate and sulphate, the estimated detection limits ranged from 2.8 to $17 \text{ ng}/\text{m}^3$). We added this information to the section describing the calibration procedure.

Line 25-28: This paragraph needs a little further explanation including references to relevant literature.

We decided to remove this paragraph, as it does not help the discussion. Indeed, we are not able to quantify the different pathways, due to the impossibility of performing a complete mass balance (see next comment), because of the lack of available standards and the remaining unidentified compounds.

Line 29-: Can you quantitatively compare functionalisation/oligomerisation pathways and fragmentation pathways without complete mass balance?

As said, we agree with the referee that it is not possible to quantify the two pathways without complete mass balance and that is what our original manuscript said. Our statement was meant in a general way, but we removed it in the revised version of the manuscript.

Page 996 line 17-18: Since glycolic acid does not seem to depend on precursor concentration, I am wondering if it could be related to background concentrations in your system. Did you investigate this e.g. in experiments with light but without TMB?

We have been performing experiments without TMB, that are not included in this manuscript. Glycolic acid concentrations reported are slightly higher than the one measured during these so-called “blank” experiments. However, it is true that the concentrations are very close to the background values. Therefore, we soften our statement in the revised manuscript. (See also comment from Anonymous Referee #2.)

Page 997: Lines 2-5: What is the uncertainty on these numbers?

The uncertainty on the normalised acid concentration is mainly the uncertainty on the aerosol phase concentration, which is roughly 30%.

Lines 12-16: The background for this statement is not clear to the reader. Please explain your reasoning.

This paragraph has been edited and should be easier to understand. The reasoning has also been modified according to comment 16 from K. Sato.

Line 17: Remove "also" in the beginning of the sentence. The whole paragraph needs editing to improve style and grammar.

This paragraph has been completely edited to improve clarity, style and grammar. See also the comments by the other referees.

Add a reference to Table 2 for the discussion of the unknown compounds.

References have been added in the revised manuscript.

page 998 line 29: Which source for the carboxylate ions do you suggest/expect?

The source of carboxylate ions in the aerosol phase would for instance be hydrolysis of ester functionalities of formed oligomers due to the dissolution in water in the aerosol collector or decomposition of PANs.

page 999 Line 2: "confirms" should read "suggests" due to the large associated uncertainties.

We agree with the referee that our statement must take into account the large uncertainties and therefore, this sentence has been edited.

Line 20-21: References are needed here.

Sato et al. (2007), for instance, observed a similar effect due to water sampling. This reference is included earlier in the text.

page 1000: The last statement only refers to the present method for determining K_p , correct?

Yes, the last statement applies especially for the presented method and this has been clarified in the revised manuscript. However, our statement may also apply to other methods determining K_p from gas phase and aerosol measurements.

Figure 3: "due to an instrumental limitation" - is it just lack of data or?

The instrumental limitation is the upper detection limit of the instrument. NO_2 is derived from the subtraction of the NO concentration from the NO_x concentration. At the beginning of the experiments with missing data, both NO and NO_x signal saturates, resulting in an incorrect NO_2 concentration (close to 0ppbv). We decided to exclude this data from the plots.

Figure 5: Why were the data not corrected for wall losses?

Wall losses are difficult to address properly and would not affect the main findings in our manuscript, as we are reporting normalised particle phase concentrations. However, the role of species lost on the smog chamber walls on partitioning coefficients is now briefly discussed.

Figure 8: In my version, the legend is in the middle of the figure, which looks odd.

As the experimental conditions are not immediately comparable between panel (b) and (d), we decided to use two different columns, while (a) and (c) differ only by the initial concentration of TMB (1200ppbv vs 600ppbv).

Please explain that the data were normalized to the total aerosol mass from SMPS data.

It is now explained in the caption of Figure 8.

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