**Atmospheric
Chemistry
and Physics
Discussions**

Interactive comment on "Evaluation of 1,3,5 trimethylbenzene degradation in the detailed tropospheric chemistry mechanism, MCMv3.1, using environmental chamber data" *by* A. Metzger et al.

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The authors thank the reviewer for his/her helpful comments. We have made changes to the manuscript in order to address these issues. Our responses to the specific comments of the reviewer are given below.

1. No indication is given of the sensitivity of the techniques used. This is especially important in the case of HONO, given its central importance, and because two different techniques were used. Also, considerable uncertainty is indicated in the PTRMS measurements of oxygenates in Figure 7. Is this a representation of the experimental variability, or of the technique – there is some discussion of a 30% uncertainty

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on page 11571, but it isn't very clear.

(a) This is a good point. Error bars are added to Figure 6 and Figure 10 (31% error bars to the IC-MS and 3-sigma precision to the PTR-MS data, 10 % accuracy for the LOPAP.)

(b) Furthermore we added an additional section to the Appendix (now Appendix B) showing a cross calibration of the PTR-MS and IC-MS technique using a nitrous acid (HONO) source and discussing the HONO concentrations as measured by PTR-MS in more detail. In addition a further figure shows calculated PTR-MS concentrations in excellent agreement with the IC-MS data for this calibration exercise.

(c) Page 11580 line 22: The following sentence was added in the discussion of Figure 7: Data from two single experiments are shown. The associated error bars correspond to the accuracy of the oxygenated VOC measurement.

2. The discussion of the phenol route on page 11573 (line25) is not very clear. The route involves either abstraction of H from the OH adduct by O2, or isomerisation of the adduct formed by reaction of O2 with the OH adduct, and elimination of HO2. What is written at present is obscure.

(a) we changed the paragraph to address this issue. Page 11573 line 25: H-abstraction from a methyl group leads to the formation of 3,5-dimethylbenzaldehyde as a first generation product while the other channels involve addition of OH and O2 to the aromatic ring. 2,4,6-trimethylphenol is formed by abstraction of an H-atom by O2 from the ring or by isomerisation of the adduct formed by reaction of O2 with the OH adduct, and elimination of HO2. The major route involves addition of O2 to the OH-adduct followed by a ring opening leading to the formation of methylglyoxal and the proposed co-products furanones...

3. The inclusion of the nitrate from reaction of the peroxy radical with NO requires comment. The peroxy radical is very short-lived and does not react with NO until [NO]

is very high. Some comment should be made on this important mechanistic detail. Was the nitrate route significant at the higher NOx conditions studied?

In this section the degradation scheme of the MCM, which we use for modeling, is described and the formation of the nitrate is included there. If this route is relevant depends on the NO concentration as mentioned by the reviewer. Some of our experiments were performed with initial NO concentrations of 300 ppb. Although this reaction route still is a very minor route at these concentrations, it should be included in Figure 1 for completeness. In our description we say that other paths are more important.

4. While equation 1 is taken from the Zador paper, some discussion and explanation would be useful. The equation would also be clearer if the second line were moved to the right and lined up with the terms on the line above to the right of the equals sign.

(a) Equation 1: was changed as suggested by the referee.

(b) The following paragraph is added to the manuscript: Thus W(HONO) is given by the gradient of the observed HONO concentration and the sources (negative terms) and sinks (positive terms) of HONO. Sources are the production via NO + OH reaction and the heterogeneous hydrolysis of NO2 at the chamber walls, while the loss is given by the HONO photolysis and the reaction with OH.

5. While the surface area of the aerosol is substantially less than the surface area of the chamber (line 16, page 11585), the aerosol is homogeneously distributed. Some assessment of the numerical feasibility of the wall mechanism (in comparison with reaction on the aerosol) should be made, e.g. by assessing the timescales of the diffusion/adsorption, wall production and diffusion into the bulk should be made. The paper says little about aerosol formation, because it is discussed elsewhere, but some comment is needed if the wall mechanism is to be supported.

The reviewer addresses the question if a wall related reaction is more likely than a reaction on the SOA surface. These points are already addressed in the manuscript.

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Most important: Under high NOx conditions (e.g. Figs 3 and 4, left panel) no! SOA is formed throughout the experiment!

(a) Page 11585 line 5: We state: The fact that HONO is already needed in the initial phase of the experiment when no secondary organic aerosol (SOA) is formed yet and under conditions where SOA formation is totally suppressed by high NOx concentrations indicates that the aerosol pathway cannot be a dominant HONO source in our system.

(b) In order to clarify this point we insert the following sentence (Page 11585 line 5): In our experiments secondary organic aerosol (SOA) formation was followed using a scanning mobility particle sizer (Paulsen et al., 2005). Under low VOC-NOx conditions (Figs 3 and 4, left panels) SOA formation is completely suppressed by high NOx concentrations throughout the experiment. Under medium VOC-NOx conditions (Figs 3 and 4 right panels and Fig. 5) nucleation occurred typically after 120-200 minutes.

(c) Section 5.3, page 11585, line 16 the following sentence is deleted from the text: The surface area of our chamber walls is typically 2-3 orders of magnitude larger than the SOA surface area.

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 11567, 2008.