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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.

A. Metzger et al.

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We would like to thank the reviewer for his/her comments and helpful suggestions. We have made changes to the manuscript in order to address these issues. Our responses to the specific comments are given below.

1. The reactions listed in Table 2 may well be familiar to an expert in chemical modelling of chamber data, but some appear to be confusing. For example, what does reaction 11 represent? Is reaction 9 a balanced chemical equation or a rate equation? (i.e. what does the superscript 2 denote?). The rate constants listed for reactions 1 and 4 are very large, are they correct? In addition, it may be useful to put in the phase of the

species i.e. (g) and (ads or w) for gaseous and adsorbed at walls respectively. More effort should be made to make this information understandable to the general reader.

We improved the table according to the reviewers suggestions! (a) Reaction 11 represents dilution due to the replenishment flow. (b) Reaction 9 represents a rate equation (c) The rate constants for reactions 1 and 4 are correct. (d) The phase of the species was added.

2. Section 4.2, product distribution: The tuned model accurately predicts the product mixing ratios for the first half of the experiment but for some of the species (especially m/z=113), there is a significant discrepancy during the latter stages. I think this requires some further comment. Is this an indication that the subsequent chemistry of some of the products is not very well known and is poorly represented in the MCM? Are some of these products transferring to the particle phase as suggested in a recent publication by the same research group (Healy et al., 2008).

The following paragraph was added to section 4.2: But especially for the m/z 113 species there is a significant discrepancy during the latter stages of the experiment. This might be an indication that the subsequent chemistry of the products is not very well known and is poorly represented in the MCM. However it should be kept in mind that an additional measurement uncertainty arises from the fact that the mass signal is not unambiguously attributable to a single compound. It might well be that the signal at m/z 113 is affected by an unknown compound or a fragment of a higher molecular weight species. Methylglyoxal and 2-methyl-4-oxopent-2-enal were identified in the aerosol phase with aerosol phase yields of 2 and 3 % respectively (Healy et al., 2008). This is unlikely to affect the gas phase measurements.

3. Section 5.3: The possibility that heterogeneous reactions could be occurring on secondary organic aerosol (SOA) generated during the experiments is considered. It is stated (page 11585, line 16) that the surface area of the SOA in the experiments is significantly less than the chamber walls. What mass or volume concentration of SOA

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was used for these calculations?

(a) 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

(b) Furthermore the following paragraph is added (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) SOA formation is completely suppressed by high NOx concentrations throughout the experiment. Under medium VOC-NOx conditions (Figs 3, 4 right and Fig 5) nucleation occurred typically after 120-200 minutes.

(c) Page 11585 line 5: We already 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.

4. Figure 10: The PTR-MS data for HONO show some fluctuation. Why is this? The following sentence is added to the manuscript: The fluctuations of the PTR-MS signal was mostly caused by instability sometimes occurring within the first 24 hours after switching from normal to HONO measuring mode.

Minor Comments

1. TMB and 1,3,5-TMB are both used as abbreviations for 1,3,5-trimethylbenzene. I suggest that the authors choose one of these abbreviations and use it throughout the whole manuscript. TMB is now used throughout the manuscript.

2. Page 11570, line 1: ethane should be ethene. Done.

3. Page 11570, lines 4-8: some literature references should be cited here to support these statements. Page 11570, lines 4-8: The following references have been added to

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the text: Therefore it was shown that O(3P) reactions become important under chamber conditions which are negligible in the atmosphere (Hynes et al., 2005; Pinho et al., 2005; Pinho et al., 2006 2007). Sensitivity studies showed that wall reactions as well as uncertainties in the photolysis rates can significantly influence the system under observation (Bloss et al., 2005a; Bloss et al., 2005b; Carter et al., 2005; Hynes et al., 2005; Pinho et al., 2005).

4. Page 11570, line 21: in-door should be indoor. Done.

5. Page 11570, line 23: 27-m3 should be 27 m3. Done.

6. Page 11571, line 12: more detail is required to describe the ozone analyser – is it a UV photometric analyser? Page 11571 line 12: We have changed the sentence to help make this point clearer: Ozone was measured by UV absorption with a commercial Environics S300.

7. Page 11571, line 25: details should be detail. Done.

8. Page 11575, line 21: where should be were. Done.

9. Page 11579, line 24: over-prediction should be under-prediction. This reviewer is not correct. Page 11579, line 24: addresses the model performance shown in figure 3 & 4 right panel: On the other hand, under medium VOC/NOx conditions the decay of TMB is fairly well simulated. The NO to NO2 conversion and the ozone production are well represented by the model in the first 1.5 h, however the model starts to over-predict the NO2 concentration followed by an over-prediction of ozone thereafter.

10. At several points in the manuscript, the tuning reaction (NO2 + light/wall = HONO) does not include the word wall (e.g. page 11580, line 1), whereas in other places it does. Surface; is now included in the descriptions of the tuning reaction throughout the manuscript: NO2 + light/surface = HONO

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