

Interactive
Comment

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.

Anonymous Referee #3

Received and published: 18 July 2008

General Comments

This paper describes the use of data obtained from atmospheric simulation chamber experiments to evaluate the atmospheric degradation mechanism for 1,3,5-trimethylbenzene (1,3,5-TMB) contained in the latest version of the Master Chemical Mechanism (MCM). A large number of experiments have been performed with various VOC-NO_x ratios and over a wide range of concentrations. In addition to measurements of VOCs, NO_x and ozone, the authors also monitored nitrous acid (HONO) during a number of the experiments and observed concentrations much higher than those pre-

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dicted by the MCM. A reaction involving the light-induced conversion of NO₂ to HONO at the chamber walls is proposed to explain these findings. The incorporation of this reaction into the MCM significantly improves the level of agreement with the experimental data.

The article is very well written and the results are presented in a clear and logical manner. The experimental and modelling data are of high quality and the interpretation and discussion of the results is appropriate. Overall, this is a very good paper which highlights the role that surface reactions play in atmospheric simulation chamber experiments. It also highlights the useful contribution that chemical models like the MCM can make to the interpretation of simulation chamber data.

I recommend publication following revision of the manuscript in line with the following comments and suggestions.

Specific Comments

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.

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).

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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 was used for these calculations?

4. Figure 10: The PTR-MS data for HONO show some fluctuation. Why is this?

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. 2. Page 11570, line 1: ethane should be ethene. 3. Page 11570, lines 4-8: some literature references should be cited here to support these statements. 4. Page 11570, line 21: in-door should be indoor. 5. Page 11570, line 23: 27-m3 should be 27 m3. 6. Page 11571, line 12: more detail is required to describe the ozone analyser; is it a UV photometric analyser? 7. Page 11571, line 25: details should be detail. 8. Page 11575, line 21: where should be were. 9. Page 11579, line 24: over-prediction should be under-prediction. 10. At several points in the manuscript, the tuning reaction ($\text{NO}_2 + \text{light/wall}$; HONO) does not include the word wall (e.g. page 11580, line 1), whereas in other places it does.

References

Healy, R.M., Wenger, J.C., Metzger, A., Duplissy, J. Kalberer, M. and Dommen, J.: Gas/particle partitioning of carbonyls in the photooxidation of isoprene and 1,3,5-trimethylbenzene, *Atmos. Chem. Phys.*, 8, 3215-3230, 2008.

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

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