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Atmospheric
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Interactive comment on "Gas phase precursors to anthropogenic secondary organic aerosol: detailed observations of 1,3,5-trimethylbenzene photooxidation" *by* K. P. Wyche et al.

Anonymous Referee #2

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This paper describes the oxidation of 1,3,5-trimethylbenzene in a large chamber. The analysis was performed using a very impressive time of flight mass spectrometer. Auxiliary measurements of O3, NOx and peroxy radicals were also made. While the major focus was on the gas phase, some physical aerosol measurements were made, and links between the gas- and aerosol-phases were developed. The use of Principal Component Analysis to identify major pathways is also very promising.

Generally, this is a very good paper, and should make a valuable contribution to the literature on this subject. A very nice feature was the use of a flowing source of NOx (using HONO photolysis); this enabled a fairly steady, low level of NOx to be maintained

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in the chamber. The other experiments, using a static mixture, suffered from the fact that the NOx changes over a wide range, and that induction periods are observed for ozone and aerosol formation. This limits the usefulness of the results in regard to the real atmosphere.

The HONO also means that the source of OH in the experiments is well characterised, and does not depend on some poorly understood wall chemistry, which is often the case.

The discussions are a little simplistic at times, especially with regard to the time profiles of the species. The authors use imprecise terms such as instability and decomposition. It is not clear whether they are referring to loss by OH, loss to aerosol, or a true unimolecular loss. The paper would be much improved if terms such as these could be made more quantitative. I think also that the authors could be more explicit in stating that the major loss of some species is to aerosol (e.g. the discussions in Section 3.8.4 and 3.10). That would save a lot of qualitative handwaving about production and loss terms.

Specific comments:

Page 11701, line 23. Should that be model, not mode?

Pages 11703-4. I disagree with the interpretation of the RO2 curves. The RO2 radicals are short-lived, and in steady state. In fact, for these conditions, the production rate of RO2 should be largely independent of the amount of VOC present, depending only on the HONO photolysis rate (this is manifested in the almost linear loss of TMB). So, an increase in the RO2 concentration will reflect a decreased loss, and a plateau will be achieved when the loss rate becomes constant, not when the rate of its production decreases.

I do not really see the relevance of Figure 3b. The ranges of concentration shown on the axes do not correspond at all with those in the experiments (either for RO2 or NO).

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Page 11705, line 15. It would be interesting to know, briefly, what Metzger et al. found, since the experiments here are inconclusive.

Page 11706, line 25: benzene is missing an e.

Fig 6. Compound (G) is missing an O-atom from the upper double bond (should be a carbonyl species).

Page 11710, line 11-17. According to the branching ratios shown in Figure 6, the compounds (D) and (W) should be formed in roughly equal yields (0.04x0.97 and 0.93, respectively). However, the reported peak concentrations differ by a factor of 10. Is this due to a difference in reactivity? The yield of 3,5-dimethylbenzaldehyde seems about right (1%), whereas I would expect the yield of 2,4,6-trimethylphenol to be similar, based on their molar yields and relative rates with OH. It would be good if time profiles of these compounds could be shown (measured and calculated), since their kinetics should be fairly simple (primary production, loss by OH). This would give the reader a lot more confidence in the more complex compounds measured in the study.

In Figure 9d and Table 4. Is the compound CH3CO3H peracetic acid or hydroxyacetic (glycolic) acid?

Section 3.8.4. I find the NO-addition experiments in Section 3.8.4 interesting, but confusing. Just how much NO was added at the end of reactions 6 and 7? It seems that the ozone is removed rapidly, but then NO2 continues to increase for quite a time, and NO is further removed. What is the mechanism for this extra NO2 production? This seems to imply the production of RO2 radicals in the dark. How about decomposition of PAN-type molecules?

Where exactly does the 265 ppb of NOx that is present in the initial mixture end up?

Looking at Figure 9, there is no strong evidence for the decay of the bridged ketone upon addition of NO, and nothing that correlates with the increase of m/z 113, contrary to what it says in the text.

Page 11717, last line. m/z 45 should be 43?

Page 11719, last line. This sentence does not seem complete.

Page 11723, line 2. Brigded should be Bridged

Table 1, header to column 4. Should be NO2, not NOb.

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