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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.

K. P. Wyche et al.

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General Comments As requested by the referee, the descriptive language within the manuscript has been altered where appropriate in order to clarify processes underlying the chemistry of the oxidation system.

Specific Comments Pages 11701, line 23: The word "mode" has been replaced with the word "method".

Pages 11703-4: The statement regarding peroxy radical behaviour interpretation has been modified in accordance with the referee's helpful comments. The following paragraph replaces the original: *"The temporal behaviour of the peroxy radicals during the low NOx experiments can be attributed to the constant HONO input and photolysis* *rate. Upon being introduced into the chamber, HONO was photolysed to yield OH and NO. Once formed OH would have reacted rapidly with the precursor CO and 1,3,5-TMB leading to the production of HO_2 and RO_2 radicals, respectively. Within the chamber matrix hydro and organic peroxy radicals would have resided in steady state, being formed and then reacted rapidly. Consequently, the rise in radical concentration observed in Figure 4 during the early stages of the experiment, indicates that up to 400 minutes HO_2 and RO_2 species were produced at a faster rate than they were consumed. The subsequent onset of plateau behaviour in radical concentration highlights the point at which the HO_2 + RO_2 loss rate became constant."*

Figure 3b: The axes of Figure 3 appear to be been mislabelled. Figures 3(a) and (b) have now been replaced with plots which express the data in a clearer manner. Both Figures 3 (a) and (b) cover the data range in question, indeed they contain data taken from experiments 6 and 7, hence both are relevant to the paper.

Pages 11701, line 23: The spelling of "benzene" has been corrected.

Figure 6: Figure 6 has been corrected; the missing O atom has been added to compound (G).

Pages 11710, line 11 - 17: The peak concentration of 2,4,6-trimethylphenol is in fact ca. 2.5 ppbV (with a mass yield ca. 3.8 percent), the 0.6 ppbV reported is an error in the original manuscript. As requested by the referee temporal profiles have now been included for compounds (D), 3,5-dimethylbenzaldehyde, and (W), 2,4,6-trimethylphenol, for both high and low NOx experiments. Modelled profiles of both compounds will be shown in our forthcoming companion paper, which focuses on MCMv3.1 simulations of the chamber experiments and includes direct comparisons with the measured data presented here.

Figure 9(d) and Table 4: The compound should be hydroxy acetic acid. This has now been clarified in the manuscript.

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Section 3.8.4: A sentence has been added to Section 3.8.4 to state the concentration of NO added to the chamber during the "dark phase". The referee is correct; a portion of the NO_2 "burst" measured during the dark phase will originate from the thermal decomposition of PAN type compounds. The following statement has been added to clarify this: *""The major fraction of the additional NO_2 measured during the dark phase clearly results from the NO + O_3 -> NO_2 + O_2 reaction. However, it is likely that NO_2 will also be liberated from the thermal decomposition of reservoir, PAN type species and initially from RO_2 + NO reactions."*

With regards to the fate of the NO_2, a statement earlier in the manuscript explains this (see Page 11, Section 3.1): *""Eventually, NO_2 is removed from the gas phase through the production of nitric acid (HNO_3) via reactions on the chamber walls and incorporation into organic nitrates and the aerosol phase."*

Figure 9: A small decrease is observed in the profile of m/z 185 (the O_2-bridged ketone) during the dark phase (e.g. see Fig. 10) of experiments 6 and 7 which is not seen in experiments which were run for longer, indeed during longer run experiments, the profile of the O_2-bridged ketone eventually reaches a lengthy plateau for showing small decay after ca. 21 hours.

Pages 11717, last line: m/z 45 is correct (acetaldehyde + a fragment ion of m/z 73, methyl glyoxal)

Pages 11719, last line: The referee is correct, this sentence is incomplete, ad indeed the end of the paragraph has been truncated; this must be due to an error in up-loading the manuscript to the ACPD web page as it reads correctly in the document submitted. The sentence (and end of the paragraph) should read: *"Subsequently methyl glyoxal, the m/z 113 species and the O_2-bridged nitrate, reached peak concentrations 170, 80 and 80 minutes later than in experiment 6, respectively. This delay and subsequent shift in concentration peak coincided with the delay in nucleation described earlier, further implicating the importance of such compounds in aerosol formation and growth."*

Pages 11723, line 2: The spelling of "bridged" has been corrected.

Table 1: Again the "b" instead of "2" must be an error in the manuscript up-load.

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 11685, 2008.

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