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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.

Anonymous Referee #1

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This is an interesting and important paper in which results on 1,3,5 trimethylbenzene (TMB) from a large number of smog chamber experiments are compared with simulations using the master chemical mechanism (MCMv3.1). Problems with comparisons of this sort have been identified in the past, and are well reviewed in this paper. Such evaluations of the MCM are particularly problematic for aromatic, and a number of potential mechanistic deficiencies have been identified, but have not been resolved. The present paper is distinctive because it includes a substantial number of experiments, so that experimental error and dependence on conditions can be examined. The major

source of error in the base case model, derived from the MCM and an assessment of chamber wall reactions, is shown to be associated with an underprediction of HONO, and hence of OH. The additional HONO source is ascribed to a photochemical reaction of NO2 on the chamber walls. Tuning of this reaction to the observed HONO resolves many of the difficulties and, in particular, increases the reactivity of the system.

The paper makes an important contribution and should be published. A number of issues should be considered by the authors:

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 on page 11571, but it isn’t very clear. 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. 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? 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. 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

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8, S5501–S5503, 2008

Interactive Comment

formation, because it is discussed elsewhere, but some comment is needed if the wall mechanism is to be supported.

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8, S5501–S5503, 2008

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