**Atmospheric
Chemistry
and Physics
Discussions**

Interactive comment on "Evaluation of detailed aromatic mechanisms (MCMv3 and MCMv3.1) against environmental chamber data" *by* C. Bloss et al.

Anonymous Referee #2

Received and published: 6 November 2004

This article provides comparisons of experimental "smog" chamber data from a series of natural sunlight irradiations of NOx-aromatic -air mixtures with predictions using an up-to-date detailed chemical mechanism (MCMv3), and discusses the resulting agreements or disagreements. The aromatic hydrocarbons studied (benzene, toluene, p-xylene and 1,3,5-trimethylbenzene) encompass a range of reactivities towards the OH radical, the only significant chemical loss process for these compounds. The important conclusion is that the MCMv3 and MCMv3.1 chemical mechanisms do not simulate the experimental data at all well, with the differences between the experimental time-concentration profiles for the aromatic, NO, NO2 and O3 depending on the particular aromatic and the VOC/NOx ratio.

A number of recent studies have investigated the reaction mechanisms and first-generation products formed from OH radical-initiated reactions of aromatic hydrocarbons (for example, Smith et al., 1998, 1999; Klotz et al., 1998, 2002; Bohn and Zetzsch, 1999; Molina et al., 1999; Bethel et al., 2000; Bohn, 2001; Volkamer et al., 2001, 2002) and the reaction mechanisms are, at least in some aspects, better known than was previously the case. However, the discrepancies highlighted in this article between detailed chemical mechanism predictions and experimental data clearly indicate that important portions of the mechanism involved with the formation of OH radicals and NO-to-NO2 conversion are still incompletely understood. For almost all of the experimental conditions studied the aromatic loss rate is underpredicted (i.e., the predicted OH radical concentrations are too low), while the maximum ozone concentrations are overpredicted (i.e., too much NO is converted to NO2). Since additional OH radical sources in the aromatic degradation chemistry are expected to involve additional NO-to-NO2 conversion, resolving these discrepancies would seem to require mutually exclusive approaches unless significant NOx sink reactions are present (and additional NOx sink reactions also remove radicals which are precursors to OH). This article hence provides a good assessment of the status of aromatic chemistry, and the results show that more work needs to be done before the atmospheric chemistry of aromatic hydrocarbons can be modeled reliably enough for photochemical air pollution purposes.

Specific comments which the authors should consider are:

1) Page 5685. While the uncertainties in the OH radical reaction rate constants are stated in Calvert et al. (2002) to be around 20-25%, Kramp and Paulson (1998) concluded that the rate constants for the reactions of OH radicals with a series of organic compounds, including toluene, m-xylene and 1,3,5-trimethylbenzene, are known to within approximately 10%. 2) Page 5685, 3 lines from bottom. The Atkinson et al. (1992) reference cited dealt with the reactions of OH radicals and NO3 radicals with phenol and the cresols. Possibly the reference that should be cited here is Atkinson

et al. (1989) concerning a product study of OH + benzene. 3) Pages 5686 and 5691. What about losses of chemicals to the chamber walls, which could be important for low volatility product species? 4) Page 5688, line 4 from bottom. I assume that "cresol" should be "cresol isomers" or o-, m- and p-cresol. 5) Page 5690, 7 lines from bottom. I assume that the calculated J(NO2) is for clear-sky conditions? This should be noted or clarified. 6) Page 5694, line 3. Were the fans used only during sample introduction or were they on continually during an experiment? 7) Page 5703. The typical dilution rate (or range of dilution rates) should be given. If, as stated in the text, the majority of the measured decrease in the benzene concentration in Figure 4 was due to dilution, then the dilution rate was close to 8% per hour, a rather high value. 8) As noted in the article, measurement of selected products (and specifically the first-generation products glyoxal, methylglyoxal and phenol/cresol) provides useful additional information for testing MCMv3. However, no yield data or comparisons of predicted vs experimental data are given for the analyses of other ring-opened products (the third group of key species; page 5708). Data for 3-hexene-2,5-dione, formed as a first generation product from the p-xylene reaction, would appear to be useful for mechanism testing, because this compound can be readily analyzed, appears well behaved in chambers, and its loss processes are understood (Calvert et al., 2002; Bethel et al., 2000; Tuazon and Atkinson, 2003). 9) Table 1. Some of the initial HONO concentrations need to be footnoted; that of 55.5 ppb (row 2) should be footnoted "b" and some notation should be given for those in rows 1, 2 and 13 (presumably "d"?). 10) Table 2. Is the process hν $\rightarrow$ NO2 to be viewed as a light-inducted offgassing of NO2 from the chamber walls?

References

Atkinson, R., Aschmann, S. M., Arey, J., and Carter, W. P. L.: Formation of ring-retaining products from the OH radical-initiated reactions of benzene and toluene, Int. J. Chem. Kinet., 21, 801-827, 1989.

Bethel, H. L., Atkinson, R., and Arey, J.: Products of the gas-phase reactions of OH

radicals with p-xylene and 1,2,3- and 1,2,4-trimethylbenzene: effect of NO2 concentration, J. Phys. Chem. A, 104, 8922-8929, 2000.

Bohn, B.: Formation of peroxy radicals from OH-toluene adducts and O2, J. Phys. Chem. A, 105, 6092-6101, 2001.

Bohn, B. and Zetzsch, C: Gas-phase reaction of the OH-benzene adduct with O2: reversibility and secondary formation of HO2, Phys. Chem. Chem. Phys., 1, 5097-5107, 1999.

Calvert, J. G., Atkinson, R., Becker, K. H., Kamens, R. M., Seinfeld, J. H., Wallington, T. J., and Yarwood, G.: The Mechanisms of Atmospheric Oxidation of Aromatic Hydrocarbons, Oxford University Press, 2002.

Klotz, B., Sørensen, S., Barnes, I., Becker, K. H., Etzkorn, T., Volkamer, R., Platt, U., Wirtz, K., and Martín-Reviejo, M.: Atmospheric oxidation of toluene in a large-volume outdoor photoreactor: in situ determination of ring-retaining product yields, J. Phys. Chem. A, 102, 10289-10299, 1998.

Klotz, B., Volkamer, R., Hurley, M. D., Sulbaek Andersen, M. P., Nielsen, O. J., Barnes, I., Imamura, T., Wirtz, K., Becker, K. H., Platt, U., Wallington, T. J., and Washida, N.: OH-initiated oxidation of benzene. Part 2. Influence of elevated NOx concentrations, Phys. Chem. Chem. Phys., 4, 4399-4411, 2002.

Kramp, F. and Paulson, S. E. : On the uncertainties in the rate coefficients for OH reactions with hydrocarbons, and the rate coefficients of the 1,3,5-trimethylbenzene and m-xylene reactions with OH radicals in the gas phase, J. Phys. Chem. A, 102, 2685-2690, 1998.

Molina, M. J., Zhang, R., Broekhuizen, K., Lei, W., Navarro, R., and Molina, L. T.: Experimental study of intermediates from OH-initiated reactions of toluene, J. Am. Chem. Soc., 121, 10225-10226, 1999.

Smith, D. F., McIver, C. D., and Kleindienst, T. E.: Primary product distribution from the

reaction of hydroxyl radicals with toluene at ppb NOx mixing ratios, J. Atmos. Chem., 30, 209-228, 1998.

Smith, D. F., McIver, C. D., and Kleindienst, T. E.: Primary product distribution from the reaction of OH with m-, p-xylene, 1,2,4- and 1,3,5-trimethylbenzene, J. Atmos. Chem., 34, 339-364, 1999.

Tuazon, E. C. and Atkinson, R.: OH radical-initiated reaction of 3-hexene-2,5-dione: formation of methylglyoxal, Environ. Sci. Technol., 37, 3339-3341, 2003.

Volkamer, R., Platt, U., and Wirtz, K.: Primary and secondary glyoxal formation from aromatics: experimental evidence for the bicycloalkyl radical pathway from benzene, toluene, and p-xylene, J. Phys. Chem. A, 105, 7865-7874, 2001.

Volkamer, R., Klotz, B., Barnes, I., Imamura, T., Wirtz, K., Washida, N., Becker, K. H., and Platt, U.: OH-initiated oxidation of benzene. Part 1. Phenol formation under atmospheric conditions, Phys. Chem. Chem. Phys., 4, 1598-1610, 2002.

Interactive comment on Atmos. Chem. Phys. Discuss., 4, 5683, 2004.