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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Consecutive reactions of aromatic–OH adducts with NO, NO_2 and O_2: benzene, toluene, m- and p-xylene, hexamethylbenzene, phenol, m-cresoland aniline" *by* R. Koch et al.

Anonymous Referee #3

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Aromatic hydrocarbons are important components of gasoline and diesel fuels, vehicle exhaust and of volatile non-methane organic compounds in urban atmospheres. Despite over two decades of study, the atmospheric chemistry of aromatic compounds is still not well understood. It is known (in part because of previous studies by this research group) that aromatics dominantly react in the atmosphere with OH radicals and that the initial OH radical reaction proceeds mainly by addition to form a hydroxycyclohexadienyl-type radical (an OH-aromatic adduct). The subsequent reactions of these OH-aromatic adducts then determine the products formed; the mecha-

nistic details of these subsequent reactions are however largely unknown.

This manuscript reports the results of experimental laboratory studies of the reactions of OH radicals with a series of aromatic compounds in the presence of varying concentrations of O2, NO2 and NO, thereby allowing rate data for the reactions of the OH-aromatic adducts with these species to be derived. While some of this work has been reported previously (in part in reports which are not readily accessible), it is gratifying to see this important body of research now being presented in the open literature. As expected from this research group, the experimental work and data analysis appears to be very thorough, and the manuscript is generally well written.

Detailed comments are:

Page 7625, line 7. “Atkinson and Arey, 2004)” should be “Atkinson and Arey, 2003)”.

Page 7625, lines 7-10. To aid the reader, the authors could note that these processes are reactions (1), (-1) and (2).

Page 7626, lines 1-6. No mention is made here of hexamethylbenzene.

Page 7628, line 21. To avoid any ambiguity, the authors could replace “40” by “40 x 103” (and similarly in a number of other places in the manuscript).

Page 7630, line 5. I suggest replacing “and S is the scavenger” by “and S is the scavenger (O2, NO2, or NO in this work)”.

Page 7630, line 20. “b = k-1c = k1[A]” needs to be replaced by “b = k-1, c = k1[A]”. Also, “d = k1 + k5 + k6[S]” should be “d = k-1 + k5 + k6[S]”.

Page 7632, line 15. Should “residua” be “residuals”?

Page 7632, line 23. I suggest replacing “skips this shaky ground” by something like “avoids this covariance problem”.

Page 7633, line 13. The authors need to include more detailed discussion of how

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the aromatic compound concentrations in the reaction cell were determined. The text suggests that the aromatic concentration, [A], was obtained from the flow rate through the saturator containing the aromatic, the total gas flow, and the vapor pressure of the aromatic at the saturator temperature. Hence an accurate knowledge of the vapor pressures of the aromatic compounds studied is needed. Some discussion of where these vapor pressure data originated, and the likely uncertainties in the vapor pressures, and hence aromatic concentrations [A], is needed.

Page 7633, line 14. I suggest replacing “except benzene and HMB” by “except for benzene and HMB”.

Page 7633, line 20. I suggest replacing “considerable” by “noticeable” or “observable”.

Page 7633, lines 23 and 24. “vpm” needs to be defined (unless it should be “ppm”?).

Page 7634, line 16. To avoid repetition, “to keep H2O2 constant” should be deleted.

Page 7635, line 21. The authors could note that Figure 1 contains data for m-cresol; i.e., “Fig. 1 shows decays obtained for m-cresol “.

Page 7636, line 13. I suggest replacing “the former result” by “the former result of Koch and Zetzsch (1994)”

Page 7636, line 21. The rate constant referred to here is presumably that for H + NO2. This should be noted.

Page 7637, line 20. I suggest replacing “skipped” by “avoided”.

Page 7639, lines 24 and 25. I suggest replacing “who came up with” by “who derived”. Also, on line 25, Perry et al. (1997) obtained an upper limit of 1 x 10-15 cm3 s-1 at 353-397 K, and I therefore suggest replacing “being less or equal to 1.0 x 10-15 cm3 s-1.” by “being $<$1 x 10-15 cm3 s-1 at 353-397 K.”

Page 7640, line 18. Delete the comma after “both”.

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Table 1. The authors should include their upper limits to the rate constants for the OH-aromatic adduct reactions with NO.

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Interactive Comment