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***Interactive comment on* “Consecutive reactions of aromatic–OH adducts with NO, NO<sub>2</sub> and O<sub>2</sub>: benzene, toluene, m- and p-xylene, hexamethylbenzene, phenol, m-cresol and aniline” by R. Koch et al.**

**Anonymous Referee #1**

Received and published: 28 August 2006

This paper reports a study of the reactions of the adducts resulting from the addition of OH to the aromatic hydrocarbons benzene, toluene, m- and p-xylene, hexamethylbenzene, phenol, m-cresol and aniline with NO, NO<sub>2</sub> and O<sub>2</sub> using the FP-RF technique. The paper is a mixture of old and new results with the older previous reported results being reworked using improved software tools. The previous work on p-xylene, m-xylene, m-cresol and aniline appears to only have been published in non-peered reviewed articles.

Although the majority of the paper appears to consist of mainly reworked data and

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the “new” factor is fairly low I still think that the manuscript deserves publication since the re-evaluation of the old data sets in combination with some new work gives more confidence in the results and the article is a nice concise review on the current status of aromatic OH-adduct chemistry. The article is generally well written and is logistically constructed. In table 1 I found it somewhat difficult to discern what data is old, new or re-evaluated, perhaps bold or italic type could be used in place of superscripts to make the difference more transparent.

The authors assign error limits to the rate data which they present in Table 1. Could they please state how the errors were derived. Without actually having personally performed the type of fitting procedure used by the authors to extract the rate constant information from their data I find it extremely difficult to judge just how much “leeway” there is in the rate information which is extracted using the fit procedure. Obviously the information that the authors extract from their data depends very much on the reaction scheme which is used to model the results. Reaction (1/-1) in the scheme is the addition of OH to the ring to form the aromatic-OH-adduct. In the case of benzene only one aromatic-OH-adduct is possible and for hexamethylbenzene only addition at the ipso position is possible, however but for the other aromatic compounds addition of OH to the ring at different positions is possible. While the results from product studies suggest that in many cases addition at one particular position will dominate the results are such that significant addition at several ring positions is possible, i.e. the aromatic-OH-adduct could well be a mixture of OH addition at the positions meta ortho, or para to ring substituents. While there is no precedent for OH gas-phase addition at ipso positions in that the ring that I am aware of there are many examples in the solution phase, e.g. Hüber and Roduner, *J. Mater. Chem.*, 1999, 9, 409-418 Richter et al., *JACS* 1983, 105, 5434-5440 Schuler et al., *J. Phys. Chem. A* 2002, 106, 12178-12183 Albarran and Schuler, *J. Phys. Chem. A* 2005, 109, 9363-9370 Peller et al., *Chem. Eur. J.* 2003, 9, 5379-5387 Ipso addition has been suggested in the gas phase reaction of NO<sub>3</sub> with phenol (Harrison et al., *Atmos. Environ.* 39 (2005) 231-248 and Bolzacchini et al., *Environ. Sci. Technol.* 35 (2001) 1791-1797) and more recently in

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the reaction of OH with polybrominated diphenyl ethers with OH Radicals (Raff and Hites, J. Phys. Chem. A, 2006, in press). DFT calculations of gas phase ipso OH addition to substituted aromatics and discussed in: Johnson et al. (J. Photochem. And Photobiol. A : Chem. 2005, 176, 98-106) Bolzacchini et al. International Conference on Air Pollution - Proceedings, 1997, pp 893-902.

My point is that the rate coefficients extracted from the experimental data for some of the compounds will be composite values of the reactions of the scavengers with all of the possible aromatic-OH-adduct isomers. My question is: if this is happening and the reaction rates at the various OH addition sites are different what effect would this have on the shape of the experiment decay profiles? If the reactions of the aromatic-OH-adducts were significantly different would the authors be able to predict this from the profile shapes? Perhaps not very much difference would be expected for the meta, ortho and para OH adducts but what about the addition at an ipso position? I am only speculating at the moment but perhaps the authors should discuss the possible formation of different aromatic-OH-adduct isomers and that they may have different reactivities toward the scavengers.

The authors have excluded reactions of type, (AOH) HCHO + RO<sub>2</sub> → products (8), as employed by Grebenkin and Krasnoperov in their C<sub>6</sub>H<sub>6</sub>OH + O<sub>2</sub> study, from their reaction scheme arguing, using benzene as an example, that such a reaction would lead to a strongly negative temperature dependence for the benzene system where they in fact observed a slightly positive temperature dependence. Is there enough experimental kinetic evidence to support such a strong statement for this type of reaction? In RO<sub>2</sub> + RO<sub>2</sub> reactions, for example, the measured rate coefficients are highly variable for different RO<sub>2</sub> and temperature dependencies between all shades of positive and negative have been observed. In RO<sub>2</sub> + HO<sub>2</sub> reactions, however, only negative temperature dependencies have been observed for the reactions thus far investigated. I find the argument with the O<sub>2</sub> saturation against the occurrence of (AOH) HCHO + RO<sub>2</sub> → products (or at least having only marginal influence) as more robust.

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At the end of the paper the authors state that the mechanism of the effective reaction of AOH + S is not clear and discuss several possibilities. For the compounds in which different aromatic-OH-adduct can be formed it will probably be extremely difficult to differentiate between the different mechanisms if the various isomers react differently.

The conclusions reached in the paper concerning the effect of NO<sub>x</sub> on the OH radical initiated oxidation of aromatics are the same as those reached in earlier studies and in this respect the paper offers no new insights into the oxidation mechanism, however, as I stated above I still consider that the revamp of the old results has been worthwhile.

“Educts” in page one appears to be a German word and is certainly not a word which finds common usage in scientific English. I did find the word in an English dictionary in which the following meaning was given: that which is educed, as by analysis. I assume, however, that in this particular case, the authors are referring to reactants.

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Interactive comment on Atmos. Chem. Phys. Discuss., 6, 7623, 2006.

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