

Interactive comment on “Consecutive reactions of aromatic–OH adducts with NO, NO₂ and O₂: benzene, toluene, m- and p-xylene, hexamethylbenzene, phenol, m-cresol and aniline” by R. Koch et al.

Anonymous Referee #2

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This paper presents new data concerning the reactions of a series of OH-aromatic adducts with O₂, NO and NO₂. These new data are of importance for modelling the oxidation of aromatics in the atmosphere. The methods are appropriate as efforts have been made for improving the technical procedures.

The authors should consider the following comments.

- Why use the photolysis of H₂O to produce OH rather than that of H₂O₂ ? Are the side reactions of H atoms with O₂, NO, NO₂, really negligible ?

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- Reactions of OH-adducts with O₂; this reaction is equilibrated near room temperature, as discussed by the authors and thus, they should state whether the equilibrium constant has been taken into account in data analysis. If yes, which value of the equilibrium constant has been taken for compounds other than benzene and toluene ?

- Reactions of OH-adducts with NO; the discrepancy between the rate constant values reported for the benzene-OH adduct by Zellner et al. (1985) and by Witte and Zetzsch (1988) has been discussed in a paper by Berho and Lesclaux (PCCP, 3, 970-979, 2001) which should be cited. Even though this paper dealt with the reaction of the benzene-H adduct with NO, it is likely that the behaviour of the OH-adduct reaction is similar. Two types of reactions were found: i) an association reaction with a rate constant of $1.8 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$, close to Zellner's value. This reaction was equilibrated in the conditions of the study and the equilibrium characteristics were described. ii) a non-reversible reaction (perhaps producing HNO + benzene) with a rate constant of about $1 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$ (close to Witte and Zetzsch's value). It is likely that the same type of reactions occur in the case of the benzene-OH adduct: the value measured by Zellner et al. may correspond to the association reaction and that measured by Witte and Zetzsch to the slower non-reversible reaction, depending on experimental conditions. This possibility should be considered.

Last paragraph of section 4.4: cite Raoult et al. (2004) rather than Estupinan et al. (2003), or both. The unimolecular reaction in competition to (-7), yielding phenol + HO₂, is much too slow to be significant (high activation energy as shown by Lay et al. and by Raoult et al.). So that the present status for benzene oxidation is that phenol is produced by a direct bimolecular reaction of the OH-adduct with O₂ and that other products are produced by unimolecular isomerisation of the OH-adduct-O₂ radical. This is not so unclear.

Table 1 : It should made clear that the reaction with O₂ corresponds to reaction (6) and not to reaction (7).

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