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Atmospheric
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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.

R. Koch et al.

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First of all we thank the referees for their careful reports, remarks and suggestions and bringing several references to our attention.

Referee #1 is interested in the leeway of the fit and how the error limits were derived. Since sources of statistical error other than shot noise of photon counts have carefully been excluded, the proper weights to calculate the sum of squares are well known from counting statistics (instead of being estimated from deviations between the data and some model). We can state that the fits were rather stiff, i.e., the sum of squares raised by more than unity on small variations of the fit parameters - small compared to other

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uncertainties: estimated effects of model imperfections (see below) and errors of gas flows, total pressure, and temperature. Only in the case of benzene (and naphthalene) the quenching of the OH signal by O_2 led to an increased total uncertainty as already mentioned in the paper (chapter 3.1).

For the majority of measurements with high signal-to-noise ratio, tiny deviations from the model reach the detection limit. Those tiny model imperfections probably include the treatment of diffusion as first-order loss process, transport of the flashlamp-irradiated volume by the flow, temperature gradients, background reactions other than simple OH loss (such as reversible addition to trace impurities), OH sources due to ozone, radical-radical reactions, adduct isomers of differing stability and reactivity (see below), equilibration of the adduct+O_2 reaction (see below), and other effects not thought of yet. Since the typical total effect was an increase of the sum of squares over its expectation value (= number of data points minus number of fit parameters) by only 50 to 100 percent, i.e. comparable to the low level of noise, it is impossible to discriminate between the effects even if only two or three of them are dominating. Thus, the influence of model imperfections on the evaluated rate constants could only be estimated. Although these effects should not be treated as statistical scatter, the estimated uncertainties resemble two standard deviations in the sense that we would be surprised if more than a few values will turn out to be outside of the given interval.

Another source of measurement errors is drift. The downward trend of the background reactivity, e.g. due to wall desorption on temperature step-ups, becomes slow enough within half an hour. On the other hand, there was an upward trend during a measurement series with naphthalene due to accumulation of sticky reaction products, which could have been avoided only by investing much more time. Diminishing traces of O_2 in the saturator system may have caused the explorative first set of decays with m-cresol and (too much) O_2 (at 324 K) to be somewhat ’incoherent’ - the result depends on which decays are included in the fit.

The cases of ipso addition of OH in the aqueous phase cited by Referee #1 can not

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easily be taken as prototype for our case, as will be detailed in the final version of our paper. We thank the referee for bringing to our attention the very recent gas-phase study of Raff and Hites (2006, DOI: 10.1021/jp0630222), who found OH addition to both brominated and ether positions.

Referees #1 and 5 are interested in the visibility of competing adduct isomers including ipso adducts, and Referee #4 supplements their remark by the argument that the number of exponential components equals the number of contributing OH-radical reservoirs. Reversible formation of two adducts, e.g., would result in triexponential decays, with - under favourable circumstances - three distinct phases: The adducts are formed in proportion to the branching ratios, until the initial OH has been consumed. In a phase of redistribution, the populations reach the final steady state, governed by the equilibrium constants (distorted by loss processes). The decay would only be biexponential if $[AOH]_1/[AOH]_2$ is time-independent, which is the case if the branching ratio of adduct formation $c_1:c_2$ equals K_{eq1}/K_{eq2}, or - taking loss processes into account - if $d_1=d_2$ (see the paper for the meaning of coefficients *a* to *d*).

Although each d_i is the sum of a *T*-dependent back-decomposition rate constant b_i and a remainder varying with [S], "not very much difference would be expected for the meta, ortho and para OH adducts", as stated by Referee #1. Our simple model was indeed sufficient to explain the decays obtained in the presence of the title aromatics. It should be stated in the final version that - without having done simulations dedicated to this question - the spread of the d_i can be estimated to be less than a factor of two (for symmetrical branching - if one adduct is formed in a large excess, the deviation may be larger). "But what about the addition at an ipso position?", Referee #1 continues. Well, extensive measurements on the trimethylbenzenes obtained by Bohn and Zetzsch (TFS/LT3-D3 status colloquium, Mainz, Germany, 1998) were not included in the present paper because of small deviations from the biexponential model with 1,3,5-trimethylbenzene in the absence of O_2, almost certainly ipso addition). The development of a global k-fit for two or more adduct isomers would be a project of its own. An explorative try (presented as a part of a poster contribution to the Bunsen Conference 2006, available at www.bayceer.uni-bayreuth.de/atchem/data/aro_ref/bunsen_poster06.ppt) showed that it may be possible to differentiate between the respective scavenger reactivities.

Furthermore, Referee #1 questions the proposed strongly negative temperature dependence of k_6 in the case of reaction (8) being operative. In order to be operative, k_8 must be close to collision frequency, which indeed has a slightly positive temperature dependence. It should be made clear in the final version that the negative temperature dependence would be due to k_{-7} diminishing RO_2, a reactant of reaction (8).

Referee #2 asked why not H_2O_2 has been used as source of OH (instead of H_2O producing also H atoms). Note that a long lifetime of OH is important for our continuous detection scheme in order to collect as many as possible fluorescence photon counts. The advantage of H_2O is that its concentration, limited by the quenching of the OH fluorescence, can be 1000x higher in our experiments than $[H_2O_2]$ would be allowed for not being the dominating sink of OH. From such low precursor concentrations, a 10-mJ/cm^2 laser pulse could produce the intended $[OH]_0$, but photolysis of other reactants would be a frequent problem. With the photolysis of water in the VUV, 0.001 mJ/cm^2 is sufficient.

The side reactions of H atoms with O_2, NO, and NO_2 are manageable. The reaction $H+NO_2$ is considered in the paper and $H+O_2$ is only a problem in cycling experiments (in the presence of O_2 and NO), for which 193-nm photolysis of N_2O in the presence of H_2O would be a better choice. H+NO is not a threat, as HNO does not lead to OH in reactions with the major reactants - note that radical-radical reactions are negligible due to the low radical concentration in our experiments.

Referee #2 asked whether the equilibration of the O_2 reaction (7/-7) has been taken into account in the data analysis. It is obvious from the differential equation (I) that this is not the case. Whether it should be taken into account will be discussed in the paper:

For benzene and toluene, the equilibrium constant is known to be so small that the equilibrium is far on the left-hand side. Although k_{-7} is somewhat uncertain, it is much faster than k_{-1} so that the steady-state approximation can be used to derive what is already obvious from Fig. 4 of Bohn and Zetzsch (1999) - that the saturation effect of the equilibrium on the effective rate constant k_6 is negligible (about 1% for benzene at 299 K, even less at higher temperatures, similar for toluene, where K_{eq} is only slightly larger). For the other aromatics of this study, the peroxy radical may be more stable, but also less O_2 was needed in the experiments. Anyway, no saturation effects have been detected in our experiments.

At atmospheric conditions, where the equilibrium is roughly balanced, the saturation effect would decrease the effective rate constant of the O_2 reaction and one could argue that the FP/RF values for $[NO_2]_{1/2}$ in Tab. 2 should be corrected accordingly. However, the situation in high-NO_x chamber experiments is more complicated, as NO may open another exit channel from the equilibrium, the RO_2+NO reaction, which probably contributed to the observed NO dependencies of [benzene-OH](t) (Bohn and Zetzsch, 1999) and of product yields from benzene (Klotz et al., 2002), but was disregarded by Suh et al. (2003) who theoretically studied the competing isomerization reaction.

In fact, we should cite Berho and Lesclaux (2001), who found a reversible benzene-H+NO-reaction and proposed a corresponding benzene-OH+NO-equilibrium to explain the discrepancy between the benzene-OH+NO rate constant of Zellner et al. (1985), 10^{-12}, and our upper limits of 10^{-14} (Zetzsch et al, 1990, now more cautiously given as $<3\cdot 10^{-14}$ in Tab.1) and $5\cdot 10^{-14}$ (Bohn and Zetzsch, 1999). The latter value, although somewhat higher than our FP/RF result, poses a threat to the proposed benzene-OH+NO equilibrium, as the conditions (temperature, NO level) are closer to those of Zellner et al., leaving no room for the proposed change in the mechanism. An alternative explanation of the observations of Berho and Lesclaux will be given in the paper. Anyway, the equilibrium would be far on the left-hand side even in high-NO_x chamber experiments.

Concluding paragraph (section 4.4): Referee #2 is probably right in that phenol is formed by direct H atom abstraction, although an aqueous-phase study on benzene-OH+O_2 by Fang et al. (Chem. Eur. J. 7, 423-429, 1995) favours phenol formation via k_7. Note that the term 'prompt HO_2' is used differently by Koch et al. (1994, yield$>$90%) and Bohn and Zetzsch (1999, yield=55%, in agreement with the recently corrected phenol yield, Volkamer et al., 2002), but never in the sense of being a product of the direct H atom abstraction. The revised conclusions will not enter this discussion, since our group made no contribution to it - and the paper is not meant as a review.

We thank Referee #4 for drawing our attention to the theoretical studies of Suh et al. (2002, 2003), though it appears that their value for k_7 (leading to the most stable peroxy isomer) is more than two orders-of-magnitude lower than the result of Bohn (2001). As is true for many earlier product studies, the recent study on m-xylene by Zhao et al. (2005) yielded no result which could be compared to those of the present paper. On the other hand, we apologize for missing the paper by Berndt and Böge on phenol (PCCP 5, 342-350, 2003), who reported a value for k_{O2}/k_{NO2}, that will be included in our Tab. 2.

We will provide explicit explanation in our conclusions, why the reactions of the OH-adducts with NO and NO_2 can be neglected in the atmosphere.

Referee #3 made highly welcome suggestions for improvements of our text and communicated a lot of typos. It should be noted clearly in the final version that the vapour pressures of the compounds have not been discussed as they do not enter the results for the title reactions.

Finally, we thank Birger Bohn to remind us that the activation energy of an overall reaction may be low, as the barrier heights on that path are to be taken relative to the first reactants. However, the unusually low pre-exponential factor of our effective k_6 is still a problem that should be discussed in the final version.

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