Atmospheric photochemistry of aromatic hydrocarbons: OH budgets during SAPHIR chamber experiments

S. Nehr^{1,2}, B. Bohn¹, H.-P. Dorn¹, H. Fuchs¹, R. Häseler¹, A. Hofzumahaus¹, X. Li¹, F. Rohrer¹, R. Tillmann¹, and A. Wahner¹

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¹Institut für Energie- und Klimaforschung, IEK-8: Troposphäre, Forschungszentrum Jülich GmbH, Jülich, Germany ²Now at: Verein Deutscher Ingenieure e.V., Kommission Reinhaltung der Luft, Düsseldorf, Germany

Correspondence to: B. Bohn (b.bohn@fz-juelich.de)

Abstract. Current photochemical models developed to simulate the atmospheric degradation of aromatic hydrocarbons tend to underestimate OH radical concentrations. In order to analyse OH budgets, we performed experiments with ben-

- ⁵ zene, toluene, *p*-xylene, and 1,3,5-trimethylbenzene in the atmosphere simulation chamber SAPHIR. Experiments were ³⁵ conducted under low-NO conditions (typically 0.1–0.2 ppb) and high-NO conditions (typically 7–8 ppb), and starting concentrations of 6–250 ppb of aromatics, dependent on OH
- ¹⁰ rate constants. For the OH budget analysis a steady-state approach was applied where OH production and destruction rates ($P_{\rm OH}$ and $D_{\rm OH}$) have to be equal. The $P_{\rm OH}$ were determined from measurements of HO₂, NO, HONO, and O₃ concentrations, considering OH formation by photolysis and
- ¹⁵ recycling from HO₂. The $D_{\rm OH}$ were calculated from measurements of the OH concentrations and total OH reactivities. The OH budgets were determined from $D_{\rm OH}/P_{\rm OH}$ ratios. The accuracy and reproducibility of the approach were assessed in several experiments using CO as a reference com-
- ²⁰ pound where an average ratio $D_{\rm OH}/P_{\rm OH}$ =1.13±0.19 was obtained. In experiments with aromatics, these ratios ranged ⁵⁰ within 1.1–1.6 under low-NO conditions and 0.9–1.2 under high-NO conditions. The results indicate that OH budgets during photo-oxidation experiments with aromatics are bal-
- ²⁵ anced within experimental accuracies. Inclusion of a further, recently proposed OH production via $HO_2 + RO_2$ reactions led to improvements under low-NO conditions but the differences were small and insignificant within the experimental errors.

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1 Introduction

Large amounts of volatile organic compounds (VOCs) are released into the earth's atmosphere from both biogenic and anthropogenic sources with an estimated global emission rate on the order of 10^{12} g per year (Piccot et al., 1992; Arneth et al., 2011). Aromatic hydrocarbons like benzene, toluene, xylenes, and trimethylbenzenes are among the most abundant organic trace constituents observed in the urban environment (Fortin et al., 2005; Johnson et al., 2010). Major emission sources of aromatics are vehicle exhaust, solvent usage, and residential wood burning (Hawthorne et al., 1988; Niedojadlo et al., 2007). Once emitted to the atmosphere, organic compounds are oxidized photochemically and are then removed by wet or dry deposition.

The self-cleaning ability of the atmosphere mainly results from the presence of OH radicals that initiate the oxidation processes of most VOCs, including aromatics (Ehhalt, 1999). The predominant primary atmospheric OH source is the photolysis of O_3 (Finlayson-Pitts and Pitts, 2000). At wavelengths below about 330 nm O_3 is photolysed to electronically excited $O(^1D)$ that subsequently may react with water vapour to give OH.

$$O_3 + h\nu \longrightarrow O(^1D) + O_2 \qquad \lambda < 330 \text{ nm}$$
 (R1)

$$O(^{1}D) + H_{2}O \rightarrow 2 OH$$
 (R2)

Only a minor fraction of $O(^1D)$ reacts with H_2O , the remainder is deactivated by collisional quenching followed by a regeneration of O_3 . Photolysis of HONO at wavelengths below about 400 nm is another important OH source, especially close to the ground and in the morning hours (Kleffmann, ⁶⁰ 2007), but also in simulation chambers like SAPHIR (Rohrer et al., 2005).

$$HONO + h\nu \longrightarrow OH + NO$$
 $\lambda < 400 \text{ nm}$ (R3)¹¹⁰

These primary photolytic production processes are necessary but insufficient to maintain an effectual OH concentration,

especially in the presence of high concentrations of VOCs. A regeneration of OH from HO₂ radicals is therefore essential: ¹¹⁵

$$HO_2 + NO \rightarrow OH + NO_2$$
 (R4)

$$\mathrm{HO}_2 + \mathrm{O}_3 \to \mathrm{OH} + 2 \mathrm{O}_2 \tag{R5}_{120}$$

⁷⁰ HO₂ can be formed photolytically (e.g. from formaldehyde), directly following the initial OH + VOC reactions (prompt HO₂), or indirectly from organic peroxy radicals (RO₂) after another reaction step involving NO:

$$OH + VOC \rightarrow RO_2$$
 (R6)¹²⁵

75 $\operatorname{RO}_2 + \operatorname{NO} \to \operatorname{RO} + \operatorname{NO}_2$ (R7)

$$\mathrm{RO} + \mathrm{O}_2 \to \mathrm{R'O} + \mathrm{HO}_2$$
 (R8)

Thus, the presence of NO leads to a propagation of the radical chain and counteracts terminating HO_2 and RO_2 self- and cross-reactions. NO itself is regenerated during daylight by

 NO₂ photolysis that is accompanied by a net O₃ production. Typically the NO Reaction (R4) is dominating while the O₃ Reaction (R5) is of minor importance because of a very small rate constant. However, at too high concentrations of NO_x, 135 OH concentrations decrease because of a terminating OH +
 NO₂ reaction.

In contrast to this concept, recent field studies in areas characterized by high biogenic VOC and low NO concentrations revealed unexpectedly high levels of OH that could not be explained by model calculations. It was speculated that

- ⁹⁰ these discrepancies are explainable by so far unaccounted $_{140}$ OH recycling processes, e.g. OH formation via RO₂ + HO₂ reactions (Lelieveld et al., 2008), unimolecular decomposition reactions of RO₂ radicals (Peeters et al., 2009; Crounse et al., 2011; Fuchs et al., 2013) and/or fast photolysis of hy-
- ⁹⁵ droperoxide compounds (Wolfe et al., 2012). Alternatively, ¹⁴⁵ a generic mechanism assuming the presence of an unknown compound acting chemically similar as NO was postulated and utilized to quantify the missing rate of OH recycling (Hofzumahaus et al., 2009). Based on a steady-state ap-
- proach for OH, Hofzumahaus et al. (2009) compared the 150 known production and destruction rates of OH by taking measured concentrations of OH, HO₂, NO and the total OH reactivity of ambient air. It was concluded that during a field campaign in the Pearl River Delta in southern China, the con-
- ¹⁰⁵ ventional OH recycling rate by $HO_2 + NO$ was too small by ¹⁵⁵ a factor of three to explain the measured OH under low-NO conditions (Hofzumahaus et al., 2009; Lu et al., 2012).

In this work, a similar, widely model-independent approach to investigate OH budgets is used for the analysis of SAPHIR simulation chamber experiments with aromatic compounds. Aromatics contributed significantly to the OH reactivity during the measurements in the Pearl River Delta (Lou et al., 2010) and potential additional OH recycling from aromatics oxidation would therefore impact the OH budget. Previous chamber experiments with aromatics indeed showed unexpectedly high OH concentrations compared to model calculations (Bloss et al., 2005a). Moreover, recent laboratory work revealed high yields of prompt HO₂ (Nehr et al., 2011, 2012) and effective OH recycling in reactions of HO₂ with aromatics-related peroxy radicals (Birdsall et al., 2010; Birdsall and Elrod, 2011):

$$\mathrm{RO}_2 + \mathrm{HO}_2 \to \mathrm{RO} + \mathrm{O}_2 + \mathrm{OH}$$
 (R9)

An OH budget investigation under the controlled conditions in SAPHIR was therefore performed with four selected monoaromatic compounds together with reference experiments with CO to evaluate the validity and the accuracy of the approach.

2 Experimental

The outdoor atmosphere simulation chamber SAPHIR at Forschungszentrum Jülich facilitates the investigation of photochemical processes under defined conditions (c.f. Karl et al., 2004; Poppe et al., 2007). The SAPHIR chamber has a cylindrical shape (18 m length, 5 m diameter, 270 m^3 volume). The chamber wall is a Teflon film that is held by a steel frame. The teflon film is chemically inert and transmits solar radiation without significant absorption (Bohn and Zilken, 2005). A shutter system allows for a rapid opening and closing of the chamber roof within about 60 s.

2.1 Analytical instrumentation

SAPHIR is equipped with a comprehensive set of analytical instruments. Measurements of experimental boundary conditions include temperature (ultrasonic anemometer), pressure (capacitive gauge), replenishment flow rate (mass flow controller), and photolysis frequencies (spectroradiometer). Measurements of trace gas concentrations include volatile organic compounds (proton transfer reaction time of flight mass spectrometry, PTR-TOF-MS), HCHO (Hantzsch reaction), HONO (long path absorption photometry, LOPAP), CO (reduction gas analysis, RGA), CO₂, CH₄, H₂O (cavity ring-down spectroscopy, CRDS), as well as NO, NO₂, and O_3 (chemiluminescence, CL). The reader is referred to previous publications for detailed information on the analytical instrumentation of SAPHIR (Wegener et al., 2007; Fuchs et al., 2010, 2012; Dorn et al., 2013; Fuchs et al., 2013, and references therein).

Table 1 provides an overview of the key instruments for this study and their performances. Briefly, the detection of OH, HO_x (sum of OH and HO_2), and RO_x (sum of OH, HO_2 and RO_2) was performed by laser-induced fluorescence (LIF)

spectroscopy (Holland et al., 2003; Fuchs et al., 2008, 2011).
 From these measurements, concentrations of HO₂ and RO_{2 210} radicals were determined. Moreover, differential optical absorption spectroscopy (DOAS) (Dorn et al., 1995; Schlosser et al., 2007, 2009) was employed for the measurement of OH radical concentrations.

The total OH reactivity k_{OH} , which is equivalent to $_{215}$ the inverse atmospheric OH lifetime, was measured by the flash photolysis/laser-induced fluorescence (FP/LIF) technique that was first realized by Calpini et al. (1999) and later

by Sadanaga et al. (2004). $k_{\rm OH}$ is a pseudo-first-order rate constant given by the following expression:

$$k_{\rm OH} = \sum_{i} k_{\rm X_i+OH}[{\rm X}_i] \tag{1}$$

[X_i] denotes the concentration of a reactive trace constituent and k_{X_i+OH} is the respective second-order rate constant. The instrument used in this work at SAPHIR was deployed in previous field campaigns and was described in detail elsewhere (Hofzumahaus et al., 2009; Lou et al., 2010). The reported k_{OH} were corrected for wall losses within the instrument that account for loss rate coefficients of typically 1.5 s⁻¹ (Nehr te al., 2012).

2.2 Materials

The SAPHIR chamber was operated with highly purified ²³⁵ synthetic air made from liquid N_2 and O_2 (99.9999%, Linde). Benzene (99.8%, Merck), toluene (99.9%, Merck),

- *p*-xylene (99.8%, BDH Prolabo), and 1,3,5-trimethylbenzene (1,3,5-TMB; 99.0%, Sigma Aldrich) were used as purchased. For experiments with elevated NO concentrations a mixture of 600 ppm of NO (99.5%, Messer Griesheim) in N₂ (99.999%) was added to the chamber. CO was used in pure (99.999%) was added to the chamber. CO was used in pure (99.999%) was added to the chamber.
- form (99.997%, Messer Griesheim). Gases were introduced 240 into the chamber using calibrated mass flow controllers. Liquids were injected by microliter syringes via a heated injection port.

2.3 Experiment procedure

- The sequence of a typical SAPHIR experiment is shown in Fig. 1 taking the photo-oxidation of 1,3,5-TMB performed on 17 June 2010 as an example. All experiments started after the chamber was flushed overnight with high purity dry synthetic air to purge trace gases below the limits of detec- 250
- tion. A fan was used to assure homogeneous mixing. In the morning, the clean chamber was humidified by flushing ultrapure water vapour (Milli-Q) from a vaporizer with a high flow of zero air into the chamber. Afterwards, the shutter system was opened and the chamber was exposed to sunlight. 255
- ²⁰⁵ Usually, no other trace gases were then added for a period of about two hours. During this so-called zero air period,

HONO was formed photolytically at the chamber walls dependent on humidity and UV radiation (Rohrer et al., 2005). Relative humidities were around 40% during the illumination periods. Photolysis of HONO is the major primary source of OH radicals in SAPHIR and therefore OH (and NO) concentrations were found to increase during this period. Moreover, the background OH reactivity that typically builds up within SAPHIR without addition of any reactants, slowly rose to about 2 s⁻¹. Subsequently, the compound of interest (CO or an aromatic hydrocarbon) was injected into the chamber. The example in Fig. 1 shows an injection of about 6 ppb of 1,3,5-TMB as reproduced by PTR-TOF-MS and the OH reactivity instrument. The resulting concentration of OH radicals in SAPHIR depended on the concentrations of OH reactants and was further modulated by solar radiation. The initial aromatics concentrations were chosen dependent on the OH + aromatics rate constants to result in starting OH reactivities of about 10 s⁻¹. This ensured that the total reactivity was dominated by the aromatic compound while it was still low enough to allow the detection of OH at good signal-to-noise ratios. After 6-8 hours of illumination the chamber shutter system was closed. Experiments with aromatics were performed under low-NO (typically 0.1–0.2 ppb after injection of aromatics) and high-NO (7-8 ppb) conditions. In the case of high-NO experiments, NO was injected 30 minutes prior to the addition of the aromatic. For low-NO experiments the source of NO was photolysis of HONO. Table 2 provides an overview of all SAPHIR experiments with aromatics utilized in this work.

3 Data analysis and results

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The OH production rate P_{OH} resulting from Reactions (R1)–(R5) is given by the following equation.

$$P_{\rm OH} = j_{\rm O(^{1}D)}[O_{3}] \times 2 f_{\rm OH} + j_{\rm HONO}[\rm HONO] + k_{4}[\rm HO_{2}][\rm NO] + k_{5}[\rm HO_{2}][O_{3}]$$
(2)

 $j_{O(^{1}D)}$ and j_{HONO} are the photolysis frequencies of Reactions (R1) and (R3), respectively. f_{OH} denotes the fraction of $O(^{1}D)$ that reacts with H₂O according to Reaction (R2). For the calculation of P_{OH} measured $j_{O(^{1}D)}$ and j_{HONO} were used and rate constants k_4 and k_5 from recent recommendations: $k_4 = 3.45 \times 10^{-12} \text{ cm}^3 \text{s}^{-1} \times \exp(270 \text{ K/T})$, $k_5 = 2.03 \times 10^{-16} \text{ cm}^3 \text{s}^{-1} \times (T/300 \text{ K})^{4.57} \times \exp(-693 \text{ K/T})$ (IUPAC, 2013). The f_{OH} typically were around 0.1 and were calculated using measured water vapour concentrations and recommend rate constants of $O(^1D)$ reactions (IUPAC, 2013).

It turned out that under all conditions P_{OH} was dominated by the NO Reaction (R4). The second most important OH source was photolysis of HONO, the contribution of which is shown in the lower panel of Fig. 1 as an example. It should be noted that in some experiments where HONO measurements were not available (Tab. 2) its concentration was estimated from the resulting OH concentration during the zero air period based on a parametrization of the HONO produc-310

tion rate in the chamber (Rohrer et al., 2005). Compared to HONO photolysis, OH production rates by O_3 photolysis and the O_3 Reaction (R5) are almost negligible under the experimental conditions employed, i.e. $[O_3] < 20$ ppb) (<50 ppb for some CO experiments).

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The OH destruction rate D_{OH} is given by the product of the total OH reactivity and the OH concentration.

$$D_{\rm OH} = k_{\rm OH} [\rm OH] \tag{3}$$

 $D_{\rm OH}$ can be calculated from only two measurements because all chemical OH losses are accounted for by the measurements of $k_{\rm OH}$. In contrast, unaccounted OH recycling processes and/or primary OH sources might be missed in $P_{\rm OH}$ calculated by Eq. (2). In any case, for a short-lived species like OH, the steady-state approximation applies under the conditions of SAPHIR experiments:

$${}_{275} \quad \frac{\mathrm{d[OH]}}{\mathrm{d}t} = P_{\mathrm{OH}} - D_{\mathrm{OH}} \approx 0 \tag{4}$$

Thus, ideally also the calculated $P_{\rm OH}$ of Eq. (2) should be ³³⁰ balanced by $D_{\rm OH}$. This analysis is independent of mechanistic details and model simulations. The only exception are the HO₂ data that were corrected for interferences caused by specific organic peroxy radicals (Nehr et al., 2011; Fuchs

²⁸⁰ by specific organic peroxy radicals (Nehr et al., 2011; Fuchs et al., 2011). However, these corrections were minor, <20% in 2010 and <5% in 2011, after technical modifications of ³³⁵ the LIF instrument that were made before the 2011 experiments (Fuchs et al., 2011). More details on this correction can be found in the appendix.

The closure of the OH budget was investigated by consulting mean $D_{\rm OH}/P_{\rm OH}$ ratios and their standard deviations ³⁴⁰ for the different experiments. For this, all experimental data were synchronized to the time grid of the instrument with ²⁹⁰ the lowest time resolution (either the OH reactivity instrument during experiments in 2010 or the DOAS instrument during experiments in 2011). For the calculation of the mean ratios, data points were weighted according to the errors for $D_{\rm OH}$ and $P_{\rm OH}$ resulting from contributions of all measured ³⁴⁵ quantities using error propagation (Tab. 1).

A total of 13 experiments performed with CO in 2010 and 2011 were evaluated as reference experiments. Some of these experiments were dedicated to investigations of compounds other than aromatics where after an about two-hour CO ref- 350

erence period the compound of interest was injected. In these cases only the CO periods were taken into account. In other experiments several injections of CO were made to cover a wider range of $k_{\rm OH}$. CO was selected as a reference compound because its photochemistry is comparatively simple. It 355

is unreactive towards all gas-phase species except OH and the only known product of this reaction is HO₂ under the conditions employed. The average of the mean ratios $D_{\rm OH}/P_{\rm OH}$ obtained in the reference experiments was 1.13±0.19. The 0.13 deviation from unity reflects the accuracy of the experimental approach. This deviation is well within the accuracy of the experimental input data and consequently the OH budget was closed for the CO experiments. The standard deviation of ± 0.19 reflects the reproducibility of single experiments. All data obtained in CO experiments are collected in Fig. 2.

The results obtained with the different aromatic compounds are listed in Tab. 3 and examples of plots of $D_{\rm OH}$ as a function of $P_{\rm OH}$ under low- and high-NO conditions are shown in Fig. 3 and Fig. 4. The mean ratios $D_{\rm OH}/P_{\rm OH}$ ranged between 0.9 and 1.6 and were again mostly greater than unity. No trend was observed for the homologous series of aromatic compounds but low-NO experiments tended to give greater ratios (1.1-1.6) than high-NO experiments (0.9-1.2). Overall, considering the result of the CO reference experiments and experimental errors, OH budgets for all aromatics compounds are regarded as closed.

In order to test the potential influence of the recently proposed OH recycling by Reaction (R9), Eq. (2) was extended accordingly.

$$P_{\rm OH}^{\star} = P_{\rm OH} + k_9 [\rm HO_2] [\rm RO_2] \tag{5}$$

Estimates of the rate constant of Reaction (R9) were taken from the literature ($k_9 = 1 \times 10^{-11}$ cm³s⁻¹, Birdsall et al. (2010)). Because the RO₂ measurements cannot distinguish between different species, the measured total RO₂ concentrations and the same rate constant k_9 were used for the calculations. Inclusion of the additional term in Eq. (5) led to somewhat smaller ratios in particular under low-NO conditions (see right hand side of Tab. 3 for a direct comparison). However, overall the differences between P_{OH}^{\star} and P_{OH} were small and merely in the range of experimental errors.

4 Discussion

The results listed in Tab. 3 show that the OH budgets during the OH-initiated degradations of aromatic compounds were reasonably balanced within experimental errors for all investigated compounds. No clear trend was observed in the OH budget analysis for the homologous series of aromatic compounds. Although the degradation mechanism of all aromatics is similar, this result is noteworthy. Because the OH rate constants increase with the degree of methylation (Calvert et al., 2002), the employed initial concentrations of aromatics were very different, e.g. about 250 ppb of benzene and 6 ppb of 1,3,5-TMB. Accordingly, the fractions of the aromatics that were degraded at the end of the experiments differed strongly. While 1,3,5-TMB was completely consumed and $k_{\rm OH}$ decreased monotonically during the course of the experiment, this was not the case for benzene where only a minor fraction was lost and k_{OH} even increased because of more reactive secondary products. Despite these differences, in the temporal evolution of the experiments, no differences

in the OH budgets analyses were found. This implies that the 415 results apply in the presence of primary and secondary OH reactants that emerge in aromatic degradation processes.

All results presented in Tab. 3 are based on OH LIF data that were available in 2010 and 2011. Using OH LIF or

DOAS measurements made no difference in the OH bud-420 get analysis which is consistent with previous experiments in SAPHIR where excellent agreement of the two OH detection techniques was demonstrated under various experimental conditions (Schlosser et al., 2007, 2009; Fuchs et al., 2012).

The agreement between P_{OH} and D_{OH} was slightly better at high NO concentrations. However, this difference should be treated with caution considering the experimental uncertainties and the fact that OH destruction and production rates

were greater by a factor of about four under high-NO con-430 ditions, mainly caused by greater OH and NO concentrations. Possible reasons for these discrepancies are measurement artefacts and additional OH recycling processes.

- Regarding the NO measurements, no problems are expected during low and high NO conditions because both con- 435 centration ranges were covered by regular calibrations using test gases. HO₂ concentrations were comparable during high and low NO conditions because HO₂ formation and destruction rates were both increased at increased NO. The same
- applies to RO₂ concentrations and associated potential dif-⁴⁴⁰ ficulties regarding RO₂-HO₂ interferences (see Appendix). $k_{\rm OH}$ was also similar at high and low NO conditions and recycling of OH from HO₂ was too slow at high NO to influence the $k_{\rm OH}$ measurements. An unaccounted primary OH
- source that is specific for SAPHIR is also unlikely because 445 that would have its greatest effect during the zero air periods when the OH budget was closed (red points in Figs. 3 and 4). However, after addition of an OH reactant under low NO conditions, OH drops strongly making these measurements more
- challenging. An unaccounted offset in the OH measurements 450 could produce the observed mismatch between OH production and destruction rates, independent of the nature of the added reactant. That could explain why the ratios for CO and aromatics were mostly greater than unity under low NO con-
- ditions. In previous LIF-DOAS comparisons no such offset 455 in the OH LIF measurements was found as mentioned above. But it has to be taken into account that also DOAS measurements are more difficult at low OH concentrations.

The differences of the ratios could also be caused by additional OH recycling via HO₂ + RO₂ reactions that gain importance under low-NO conditions. Such radical-radical reactions that are usually thought to produce non-radical products can lead to enhanced OH recycling as shown by recent 460 laboratory studies for reactions of carbonyl-containing RO₂

⁴¹⁰ radicals with HO₂ (Hasson et al., 2004; Jenkin et al., 2007, 2008, 2010; Dillon and Crowley, 2008; Hasson et al., 2012; Gross et al., 2014). Recently also OH formation for the reaction of HO₂ with bicyclic peroxy radicals from aromatic ⁴⁶⁵ precursors was proposed with a rate constant k_9 as used in

the previous section. This rate constant corresponds to an OH yield of about 0.5 (Birdsall et al., 2010; Birdsall and Elrod, 2011) in agreement with a conservative upper limit of 0.5 estimated previously for bicyclic peroxy radicals from benzene (Jenkin et al., 2007). However, this upper limit may have to be scaled down further in view of recent results (Jenkin, 2014) and consequently the importance of this OH source is highly speculative. In our present work, the influence of the HO₂ + RO₂ reactions could only roughly be quantified in $P_{\rm OH}^{\star}$ by using the measured total RO₂ concentrations and the same estimated rate constant k_9 from the literature. Despite these uncertainties the small effects were found to have the right magnitude and to go in the right direction. Our data are therefore not in contradiction with the proposed additional OH recycling but cannot confirm it quantitatively. In any case, RO₂ + HO₂ reactions played a minor role for the OH budget even under the low-NO conditions of this work.

Current explicit degradation schemes of the Master Chemical Mechanism (MCMv3.2) underestimated OH radical concentrations in previous environmental chamber studies of aromatic compounds (Bloss et al., 2005a,b). This mismatch between simulated OH concentrations and those indirectly inferred from the decay rates of aromatic reactants was attributed to potentially missing OH production processes (Wagner et al., 2003). Our straightforward experimental investigation of the radical balance, however suggests that so far unaccounted OH production reactions are not likely a reason for this OH underprediction. Rather there seems to be an overestimation of OH reactivities of secondary products and an underestimation of peroxy radical concentrations in these model simulations as will be discussed in more detail in a companion publication (Nehr et al. (2014), manuscript in preparation).

The high and low NO concentrations employed in this work roughly corresponded to the conditions encountered in the Pearl River Delta field study during morning and afternoon hours, respectively (Hofzumahaus et al., 2009). While in the field campaign a strong mismatch between OH production and destruction rates by a factor of three was obtained for low-NO conditions, only an insignificant difference was observed here as discussed above. This clearly shows that the presence of aromatic compounds plays no role for the explanation of these field observations.

5 Conclusions

OH production and destruction rates, exclusively calculated from measured quantities, were determined for the first time during SAPHIR atmosphere simulation chamber experiments with the aromatic hydrocarbons benzene, toluene, p-xylene and 1,3,5-trimethylbenzene. A widely model-independent, steady-state approach for OH was used for an OH budget determination. Considering primary OH production and recycling reactions by photolysis and HO₂ 6

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+ NO, measured OH destruction rates slightly exceeded OH $_{520}$ production rates by factors ranging between 1.2 and 1.6 under low-NO conditions (0.1–0.2 ppb of NO) and 0.9–1.2 un-

⁴⁷⁰ der high-NO conditions (7–8 ppb of NO). CO reference experiments show that the OH budgets were balanced within the accuracy of this analysis. Further OH production in RO_2^{525} + HO₂ reactions that have recently been proposed in the literature may be operative but turned out to be insignificant within experimental error under the conditions of this work.

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Fig. 1. Measurements of selected quantities performed during a low-NO SAPHIR experiment with 1,3,5-TMB on 17 June 2010. Grey shaded areas indicate time periods when the chamber roof was closed. Formation of HONO, the major OH precursor in SAPHIR, was observed by LOPAP just after the humidified chamber was exposed to sunlight (red points, upper panel). The injection of 1,3,5-TMB, marked by the vertical dashed line, was observed by PTR-TOF-MS (black points, upper panel) and the OH reactivity instrument (blue points, second panel). OH and NO rapidly decreased whereas HO₂ increased after the 1,3,5-TMB addition (middle panels). Diurnal profiles of P_{OH} and D_{OH} (lower panel) were calculated according to Eqs. (2) and (3). Other data in the lower panel show the main terms contributing to P_{OH} .

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observable	method	time resolution / s	1σ precision	accuracy / $\%$
OH	Laser-induced fluorescence (LIF)	47	$0.3 \times 10^{6} \mathrm{cm}^{-3}$	10
HO_2, RO_2	Laser-induced fluorescence (LIF)	47	$1 \times 10^7 \mathrm{cm}^{-3}$	10^a
OH	Differential optical absorption spectroscopy (DOAS)	205	$0.8 \times 10^{6} \mathrm{cm}^{-3}$	6.5
$k_{\rm OH}$	Flash photolysis/Laser-induced fluorescence (FP/LIF)	180	$0.3 \ {\rm s}^{-1}$	5
NO	Chemiluminescence (CL)	90	0.005 ppb	7

Table 1. Properties of key instruments for the investigation of OH budgets during SAPHIR experiments.

^a RO₂ interference effects not included, see text

Table 2. Compilation of SAPHIR experiments with starting concentrations of aromatic hydrocarbons ([aromatic]₀). These concentrations were calculated from the initial increase of k_{OH} upon addition of reactants using OH rate constants from MCMv3.2. [NO]max denotes peak NO concentration during the experiments. Temperatures are mean values covering the experiment periods after injection of aromatics. Error bars correspond to minimum and maximum temperatures.

Table 3. Analysis of OH budgets during SAPHIR experiments. Means and standard deviations of the ratios $D_{\rm OH}$ / $P_{\rm OH}$ and $D_{\rm OH}$ / $P_{\rm OH}^{\star}$ calculated from measurements according to Eqs. (2) and (5), respectively. The data evaluation was restricted to time periods where the chamber was illuminated and aromatic OH reactants were present. N denotes the number of data points.

date	[aromatic] ₀ / ppb	[NO] _{max} / ppb	Т / К
benzene			
$07.06.2010^{b}$	230	0.75	299±2
23.06.2010	235	0.55	303 ± 3
01.08.2011	250	0.20	299 ± 5
$08.06.2010^b$	235	7.6^{a}	297 ± 3
25.06.2010	215	7.6^{a}	304 ± 2
toluene			
$05.07.2010^{b}$	65	0.46	300±4
04.08.2011	107	0.27	305 ± 4
13.06.2010	60	7.1 ^{<i>a</i>}	297±3
<i>p</i> -xylene			
14.06.2010	26	0.35	301±3
02.07.2010	26	0.35	311±3
07.08.2011	29	0.35	298 ± 2
16.06.2010	24	6.9^a	299±3
30.06.2010	24	7.1^{a}	308 ± 2
1,3,5-TMB			
17.06.2010	6.0	0.48	298±3
01.07.2010	6.5	0.45	308 ± 3
10.08.2011	7.2	0.26	$298{\pm}4$
$21.06.2010^{b}$	6.0	7.2^{a}	295±1
28.06.2010	6.5	7.6^{a}	$308{\pm}1$

date	N	$D_{\rm OH}/P_{\rm OH}$	$D_{\rm OH}/P^{\star}_{\rm OH}$
benzene			
07.06.2010	98	$1.34{\pm}0.32$	$1.28 {\pm} 0.29$
23.06.2010	118	$1.32{\pm}0.37$	1.22 ± 0.33
01.08.2011	51	$1.48 {\pm} 0.31$	$1.44{\pm}0.29$
08.06.2010 ^a	105	$0.92 {\pm} 0.22$	$0.91 {\pm} 0.22$
25.06.2010 ^a	101	$0.92{\pm}0.60$	$0.90 {\pm} 0.56$
toluene			
05.07.2010	107	$1.42{\pm}0.29$	$1.14{\pm}0.22$
04.08.2011	35	$1.56 {\pm} 0.68$	$1.37 {\pm} 0.49$
13.06.2010 ^a	53	$1.17{\pm}0.34$	$1.01 {\pm} 0.20$
<i>p</i> -xylene			
14.06.2010	71	$1.60 {\pm} 0.35$	$1.29 {\pm} 0.29$
02.07.2010	78	$1.52{\pm}0.37$	$1.09 {\pm} 0.25$
07.08.2011	15	$1.59 {\pm} 0.61$	$1.44{\pm}0.51$
16.06.2010 ^a	53	$1.12 {\pm} 0.31$	$1.01 {\pm} 0.20$
30.06.2010 ^a	50	$1.05 {\pm} 0.47$	$0.89 {\pm} 0.17$
1,3,5-TMB			
17.06.2010	68	$1.23 {\pm} 0.26$	$1.07 {\pm} 0.18$
01.07.2010	52	$1.09{\pm}0.18$	$0.69 {\pm} 0.13$
10.08.2011	41	$1.30 {\pm} 0.40$	$1.02 {\pm} 0.20$
21.06.2010 ^a	67	$1.04 {\pm} 0.22$	$1.01 {\pm} 0.19$
28.06.2010 ^a	12	$1.11 {\pm} 0.11$	$0.99{\pm}0.10$

^a high NO experiment

^b no HONO measurements available

^a high-NO experiment



Fig. 2. Correlation of OH destruction rates (D_{OH}) and production rates (P_{OH}) from all SAPHIR experiments with CO in 2010 and 2011. The solid line corresponds to a mean ratio of 1.13, the dashed line indicates a 1:1 ratio. The total number of data points is 776.



Fig. 3. Correlation of OH destruction rates (D_{OH}) and production rates (P_{OH}) for SAPHIR experiments in 2010 under low-NO conditions (upper panels) and high-NO conditions (lower panels). Black and red data points indicate different periods of the experiments. Red: zero air period; Black: after the injection of aromatics. The solid lines correspond to the mean ratios listed in the third column of Tab. 3 (P_{OH} calculated by Eq. (2)), dashed lines are 1:1 lines.



Fig. 4. Correlation of OH destruction rates (D_{OH}) and production rates (P_{OH}) for SAPHIR experiments in 2010 under low-NO conditions (upper panels) and high-NO conditions (lower panels). Black and red data points indicate different periods of the experiments. Red: zero air period; Black: after the injection of aromatics. The solid lines correspond to the mean ratios listed in the third column of Tab. 3 (P_{OH} calculated by Eq. (2)), dashed lines are 1:1 lines.

730 Appendix A

Correction of HO₂ measurement interferences

The LIF technique can only detect OH radicals. Measurements of HO₂ and RO₂ radicals by LIF work via conversion to OH upon addition of NO. The HO₂-to-OH conversion is ⁷³⁵ direct and can be made shortly before the excitation of OH within the expansion of the sample gas (Holland et al., 2003). In contrast, RO₂ has to be converted to HO₂ first which requires at least one additional O₂ reaction following the RO₂ + NO reaction. This RO₂-to-HO₂ conversion is accomplished

- ⁷⁴⁰ in a pre-reactor (Fuchs et al., 2008). The different reaction times thus allow a distinction between OH from HO₂ and RO₂. However, dependent on the nature of the RO₂ radicals this distinction is not complete because some RO₂ produce HO₂ too rapidly. Therefore, LIF HO₂ measurements, [HO₂^{*}],
- have to be corrected for the concentration of a number of interfering RO₂ radicals, $[RO_2]_i$, detected with the corresponding relative sensitivities $\alpha^i_{RO_2}$ to obtain the true HO₂ concentration, [HO₂] (Fuchs et al., 2011; Lu et al., 2012).

$$[\text{HO}_2] = [\text{HO}_2^*] - \sum_i \alpha_{\text{RO}_2}^i [\text{RO}_2]_i$$
(A1)

⁷⁵⁰ Accordingly, the true RO₂ concentration (excluding RO₂ that form no HO₂ at all), [RO₂], is given by the sum of the RO₂ concentration measured by LIF, [RO₂^{*}], plus the contribution of those RO₂ radicals, $\alpha_{RO_2}^i \times [RO_2]_i$, that were spuriously detected as HO₂.

⁷⁵⁵
$$[\mathrm{RO}_2] = [\mathrm{RO}_2^*] + \sum_i \alpha_{\mathrm{RO}_2}^i [\mathrm{RO}_2]_i$$
 (A2)

For peroxy radicals formed secondarily following the OH + benzene reaction, relative detection sensitivities compared to that for HO₂ of $\alpha_{\text{RO}_2}^{\text{benzene}} = 0.86$ were determined experimentally in 2010. In 2011, $\alpha_{\text{RO}_2}^{\text{benzene}}$ was then reduced to 0.17 by means of technical changes of the experimental setup (Fuchs et al., 2011).

Speciated RO_2 measurements were not available and consequently, the correction of the LIF data was made on the basis of numerical MCMv3.2 simulations. More details on these simulations are given elsewhere (Nehr et al., 2014). Individual organic peroxy radical concentrations, $[RO_2]_i$, were calculated for each SAPHIR experiment. Organic peroxy radicals involved in the photo-oxidation of aromatics and detectable by LIF are listed in Tab. A1. $\alpha_{RO_2}^{\text{benzene}}$ was used for the corrections according to Eqs. (A1) and (A2) for all

 $[RO_2]_i$. Additional MCMv3.2 based factors c_{RO}^i and $c_{HO_2}^i$ that account for the yields of RO in Reaction (R7) and the yields of HO₂ in Reaction (R8), respectively were also considered. Regarding the P_{OH} - D_{OH} relationships the correction of the probability of HO₂ in Reaction (R8), respectively were also considered.

tions of HO₂ concentrations finally led to ratios $D_{\rm OH}/P_{\rm OH}$ that were greater by 0.17±0.12 for the 2010 data and by 0.05±0.03 for the 2011 data. **Table A1.** Organic peroxy radicals (MCM specific designation) detectable but not discriminable by LIF and their respective RO yields $(c_{\rm RO})$ in RO₂ + NO reactions and subsequent HO₂ yields $(c_{\rm HO_2})$ in RO + O₂ reactions as implemented in MCMv3.2.

		ne .	\$° \	ene ,	TMB	
RO ₂ species	bent	rolue	Prth	ر ^ک ی ک	c _{RO}	$c_{\rm HO_2}$
BZBIPERO2	×				0.92	1.00
BZEMUCO2	×				0.90	0.50
C5DIALO2	×				1.00	1.00
PHENO2	×				1.00	1.00
HCOCO3	×	×	×	×	1.00	1.00
HOCH2CO3	×	×	×	×	1.00	1.00
MALDIALCO3	×	×			1.00	1.00
C3DIALO2	×	×			1.00	1.00
MALDIALO2	×	×			1.00	1.00
NBZFUO2	×	×			1.00	0.50
BZFUO2	×	×			1.00	1.00
HCOCOHCO3	×	×	×		1.00	1.00
NCATECO2	×				1.00	1.00
C5CO2OHCO3	×				1.00	1.00
C4CO2DBCO3	×				1.00	1.00
C6H5CH2O2		×			0.90	1.00
TLBIPERO2		×			0.89	1.00
CRESO2		×			1.00	1.00
TLEMUCO2		×			0.90	0.50
C615CO2O2		×			1.00	1.00
C5C01402		×	×		1.00	0.17
C3MCODBCO3		X	X		1.00	1.00
MC3CODBCO3		X	X		1.00	0.65
C4M2ALOHO2		×	×		1.00	1.00
C5DICARBO2		×			1.00	1.00
TLFUO2		×			1.00	1.00
MNCATECO2		×			1.00	1.00
PXYFUO2		×			1.00	1.00
CO2H3CO3		×	×	×	1.00	1.00
C6CO2OHCO3		×			1.00	1.00
PXYLO2			×		0.90	1.00
PXYBIPERO2			×		0.86	1.00
PXYMUCO2			×		0.83	0.50
C6M5CO2O2			×		1.00	1.00
PXYOLO2			×		1.00	1.00
C3MDIALO2			×	×	1.00	1.00
DMKOHO2			×		1.00	0.30
PXYFUO2			×		1.00	1.00
C4CO2O2			×		1.00	0.50
CHOMOHCO3			×	×	1.00	1.00
PXNCATECO2			×		1.00	1.00
TL4OHNO2O2			×		1.00	1.00
C6MOHCOCO3			×		1.00	1.00
C5DBCO2CO3			×		1.00	1.00
TMBO2				×	0.90	1.00
TM135BPRO2				×	0.84	1.00
TM1350L02				×	1.00	1.00
TM135MUCO2				×	0.94	0.50
C5MCO2OHO2				×	1.00	1.00
MXYFUO2				×	1.00	1.00
C4COMOHCO3				×	1.00	1.00