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Gas-phase reaction of OH radicals with benzene: products and mechanism

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The gas-phase reaction of OH radicals with benzene was studied in O_2/He mixtures under flow conditions in the temperature range 276-353 K and at pressures of 100 and 500 mbar using on-line FT-IR spectroscopy and GC-MS measurements. The reaction conditions were chosen so that the initially formed OH/benzene adduct predominantly reacted either with O_2 or O_3 . Under conditions of a predominant reaction of the OH/benzene adduct with O_2 the product formation was studied for variable NO concentrations. Identified products were the isomers of hexa-2,4-dienedial, phenol, nitrobenzene, p-benzoquinone and glyoxal. Furan was found in small amounts. For increasing NO concentrations there was a decrease of the phenol yield and the yields of trans, trans-hexa-2,4-dienedial and nitrobenzene increased, resulting in maximum values of 0.36 ± 0.02 and 0.11 ± 0.02 , respectively (100 mbar, 295 K). The *p*-benzoquinone yield of 0.08 ± 0.02 was found to be independent of the NO concentration. The temperature dependence of the phenol yield was measured in the range of 276–353 K for initial ratios of $[NO]/[O_2] = 1-20 \times 10^{-6}$ at 500 mbar. For a fixed $[NO]/[O_2]$ ratio, a distinct increase of the phenol yield with increasing temperature was observed; initial $[NO]/[O_2] = 1-1.2$ \times 10⁻⁶, phenol yield: 0.18 \pm 0.04 (276 K) and 0.68 \pm 0.05 (353 K). Generally, the total yield of carbonylic substances was found to be anti-correlated to the phenol yield. When the OH/benzene adduct reacted with O₃, trans,trans-hexa-2,4-dienedial, phenol and formic acid were identified as main products with formation yields of 0.28 ± 0.02 , 0.20 ± 0.05 and 0.12 ± 0.02 , respectively (100 mbar, 295 K). Further products were p-benzoquinone, CO and unidentified carbonylic substances. For the different experimental conditions, reaction mechanisms are proposed explaining the formation of the observed products. A simple model describing the temperature and NO_x-dependence of the phenol yield is presented.

Introduction

Benzene and a series of alkylated derivatives (toluene, xylenes, *etc.*) are predominantly emitted into the atmosphere by human activities (traffic, solvent use). In urban areas, atmospheric mixing ratios up to 30 ppb have been measured.¹ Under atmospheric conditions, the degradation process of benzene is initiated exclusively by the attack of OH radicals, forming mainly the OH/benzene adduct radical.

$$OH + \bigcirc \longrightarrow \bigcirc (1/-1)$$

The abstraction pathway forming H_2O and a phenyl radical is of less importance and accounts for 5% of the overall reaction at 298 K.^{2,3}

$$OH + + + H_2O$$
 (2)

The kinetics of the pathways (1), (-1) and (2) has been the subject of several investigations and precise data exist.^{3–5} From Arrhenius expressions³ the following rate constants for 298 K can be given: $k_1 = 1.1 \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹, $k_{-1} = 1.9$ s⁻¹ and $k_2 = 4.7 \times 10^{-14}$ cm³ molecule⁻¹ s⁻¹. The atmospheric fate of the resonance stabilized OH/benzene

adduct radical is governed by the reaction with O_2 .⁶ Recently, a kinetic study was published proposing a reversible reaction of O_2 with the OH/benzene adduct radical (for simplification only the addition in the *ortho* position is shown)

$$\overset{OH}{\longleftarrow} \overset{OH}{\longleftarrow} \overset{OH}{\longleftarrow} \overset{OH}{\longleftarrow} \overset{OH}{\longleftarrow} \overset{OH}{\longleftarrow} \overset{OH}{\longleftarrow} \overset{O(3/-3)}{\longleftarrow}$$

as well as an additional irreversible process. 7 The latter can be explained by an irreversible reaction of $\rm O_2$ with the OH/ benzene adduct radical

$$\overset{OH}{\longmapsto} \longleftrightarrow \overset{OH}{\longmapsto} \overset{O2}{\longrightarrow} \text{ products}$$
 (4)

and/or a unimolecular reaction of the formed OH/benzene adduct-O_2 radical.⁷

$$(5)$$

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For a temperature of 297 ± 2 K, a rate constant $k_3 = 2 \pm 1 \times 10^{-15}$ cm³ molecule⁻¹ s⁻¹ was estimated and the equilibrium constant $K_3 = k_3/k_{-3}$ is given as $K_3 = 2.7 \pm 0.4 \times 10^{-19}$ cm³ molecule⁻¹.⁷ Also as a result of the recently published study,⁷ the rate constants for the overall consumption of OH/benzene adduct radicals by O₂, $k_{overall} = k_4 + K_3k_5$, was determined to be $2.1 \pm 0.2 \times 10^{-16}$ cm³ molecule⁻¹ s⁻¹. This value is in line with former published data from the same group.⁶

Nevertheless, the first stable products of the overall reaction of O₂ with the OH/benzene adduct radical are still uncertain. Klotz *et al.*⁸ proposed the formation of benzene oxide/oxepin as the primary product of the reaction of O₂ with the OH/ benzene adduct radical, contrary to a theoretical prediction.⁹ The identification of benzene oxide/oxepin was the subject of a former investigation from this laboratory.¹⁰ As a result of this experimental study, performed under flow-tube conditions without NO_x additions in the pressure range 13–100 mbar, $[O_2] = 1-16 \times 10^{17}$ molecule cm⁻³, the formation of benzene oxide/oxepin was found to be negligible, yield: <0.03 (FT-IR analysis) and <0.01 (GC-MS analysis).¹⁰



Identified products from the reaction of OH radicals with benzene resulting from chamber studies are glyoxal,¹¹ nitrobenzene¹² and phenol.^{12–14} The formation yields for phenol are quite different, 0.236 ± 0.044 ,¹² 0.26 ± 0.05^{13} and 0.50 ± 0.05 ,¹⁴ indicating the influence of experimental conditions on the product yields. As a result of a flow-tube study without NO_x additions at 100 mbar, phenol was found with a yield of 0.23 ± 0.07^{10} to be in line with the lower yields from the chamber experiments. Besides CO, formic acid and *p*-benzoquinone, unidentified carbonylic substances (yield: 0.59 ± 0.11) represented the main product fraction under the flow conditions used.¹⁰

Generally, knowledge concerning the main pathways occurring in the OH radical initiated oxidation of benzene in the atmosphere and the resulting product distributions is sparse. The subject of this work is to determine the first stable products from the reaction of OH radicals with benzene under different experimental conditions. To come close to atmospheric conditions, the pressure range of the flow experiments was extended to 500 mbar, allowing O₂ concentrations of 8×10^{18} molecule cm⁻³. In a recently published kinetic study of the reaction of O₂ with the OH/benzene adduct⁷ a distinct temperature dependence of the product distribution in the range of atmospheric temperatures was discussed. The temperature dependent measurements in the range of 276–353 K within the present study should help to clarify this fact.

Furthermore, the subject of a second part was a product study concerning the reaction of the OH/benzene adduct radical with O_3 . Because the reaction of the OH/benzene adduct radical with O_2 is relatively slow, at least under highly polluted conditions the reaction of O_3 can be in competition with the O_2 reaction. To the authors' knowledge there are no experimental studies in the literature concerning the kinetics as well as the product distribution for the reaction of the OH/ benzene adduct radical with O_3 .

Experimental

The gas-phase reaction of OH radicals with benzene was investigated in different He/O_2 mixtures under low-flow conditions using on-line FT-IR spectroscopy and GC-MS measurements as analytical techniques. Two series of experiments

were carried out: (i) at a total pressure of 100 mbar at room temperature (295 ± 2 K, flow tube: 1.8 cm i.d. quartz glass) and (ii) at a total pressure of 500 mbar in the temperature range of 276–353 K using a flow tube surrounded with a thermo-jacket (1.8 and 4.0 cm i.d. quartz glass). A schematic of the experimental set-up is given in Fig. 1.

For on-line FT-IR analysis, the main part of the reaction gas was pumped continuously through a 2050 cm³ cell with a White cell mirror system (optical path length 10 m). FT-IR spectra were recorded with an instrumental resolution of 8 cm⁻¹ using a MCT detector by coadding of 200-3000 scans (Nicolet Magna 750). Benzene, phenol, nitrobenzene and formic acid were identified by characteristic band locations and the concentrations were determined using calibrated spectra of authentic samples. The three isomers of hexa-2,4dienedial and p-benzoquinone are solids. Because of their low sublimation vapour pressure, a determination of the absorption cross section under the experimental conditions used here was impossible. Reference spectra of these compounds were recorded by flushing out the gas phase over a solid sample by the carrier gas. For the cross section of the carbonyl absorption of these species the value for the structurally similar cisbutenedial, obtained from this laboratory, of 7.9 ± 0.4 $\times 10^{-19}$ cm² molecule⁻¹ (base 10) was used in each case.¹⁵ For cis.trans- and trans.trans-hexa-2.4-dienedial, approximated cross sections for the carbonyl absorption measured in a heatable cell at 355-385 K with an instrumental resolution of 1 cm⁻¹ are reported in the literature to be 2.4×10^{-18} cm² molecule⁻¹ each (base e).¹⁶ This value is approximately 30% higher compared to that of cis-butenedial, representing a rough estimate for the uncertainty of the concentrations of the hexa-2,4-dienedials and p-benzoquinone in the present study. To estimate the concentration of unidentified carbonylic substances, an averaged integrated band intensity (IBI) for the carbonyl absorption (1690-1780 cm⁻¹) of 7.9×10^{-18} cm molecule⁻¹ was taken, derived from methyl ethyl ketone $(7.8 \pm 0.3 \times 10^{-18} \text{ cm molecule}^{-1})$, methyl vinyl ketone $(7.4 \pm 0.1 \times 10^{-18} \text{ cm molecule}^{-1})$ and methacrolein $(8.4 \pm 0.1 \times 10^{-18} \text{ cm molecule}^{-1})$. All product yields were determined with reference to reacted benzene, yield = $[product]/\Delta[C_6H_6].$

Furthermore, a small gas stream was pumped continuously through a GC loop for MS analysis (HP 5890 with HP-MSD 5971) using an additional pump system. The heated sample loop was directly connected with the outlet of the flow tube by a heated transfer line. A 30 m, 0.25 mm i.d. column (HP 5MS) for standard analysis and a 25 m, 0.32 mm i.d. column (Chrompack Poraplot Q) for highly volatile compounds were chosen for product separation.

In addition, for identification of produced carbonylic substances the derivatisation technique using PFBHA¹⁷ (O-(2,3,4, 5,6-pentafluorobenzyl)hydroxylamine hydrochloride) with subsequent GC-MS analysis (HP 6890 with HP-MSD 5973) was carried out. For this purpose, the reaction gas was pumped through a cooled trap maintained at liquid argon temperature. After disconnecting the trap from the flow tube,



Fig. 1 Schematic of the experimental set-up.

The pressure in the flow tube and in the cell for FT-IR analysis was monitored by capacitive manometers (Baratron). Before each series of experiments, a thermocouple was introduced in the reaction zone to monitor the temperature. All gas flows were set by calibrated mass flow controllers (MKS 1259). For the total pressure of 100 mbar the gas flow was 2500 standard cm³ min⁻¹, resulting in a bulk velocity of 1.8 m s^{-1} and a residence time of 0.25 s. For the experiments at 500 mbar the gas flow was set at 7500 standard cm³ min⁻¹ and the bulk velocities ranged from 0.2 to 1.2 m s⁻¹ (residence time: 0.37-2.5 s) dependent on the temperature and the flow tube used. In all experiments, benzene was used in large excess to prevent consecutive reactions of products with OH radicals, $[C_6H_6] = 1.9-3.8 \times 10^{15}$ molecule cm⁻³. The amount of converted benzene was in the range $2.3-14.6 \times 10^{12}$ molecule cm^{-3} . OH radicals were produced via the reaction sequence:

$$H + O_2 \rightarrow HO_2 \tag{7}$$

$$HO_2 + NO \rightarrow OH + NO_2$$
 (8)

or in the presence of O_3 via:

$$H + O_3 \rightarrow OH + O_2 \tag{9}$$

Pathway (9) produces vibrationally excited OH radicals with $v \leq 9$. The excited OH radicals undergo nonreactive collision relaxation via:

$$OH(v) + M \to OH(v - 1) + M$$
(10)

The rate constant $k_{10}(M, v)$ for the main components of the carrier gas in these experiments was reported to be $<10^{-14}$ cm³ molecule⁻¹ s⁻¹ (M = He, v = 2).¹⁸ Thus, the life time of OH(v = 2) with respect to collision relaxation with He at 100 mbar is $>4 \times 10^{-5}$ s. By analogy with other colliders, for OH(v > 2) a more efficient relaxation process can be expected. With an initial benzene concentration of 3.8×10^{15} molecule cm^{-3} in these experiments, the life time of ground state OH radicals with respect to reaction (1) is 2.1×10^{-4} s (k_1 (298 K) = 1.23×10^{-12} cm³ molecule⁻¹ s⁻¹ (ref. 2)). Therefore, reactions of excited OH radicals with benzene, at least in part, can not be ruled out.

The H-atoms were produced in a 0.8 cm i.d. moveable duran-glass tube by means of a microwave discharge (SAIREM GMP 03 K/SM) operating at 50-70 W using 0.004-0.064% H₂ diluted in He.

The gases used had stated purities as follows: He (99.999%), O2 (99.9996%) (Linde), H2 (99.999%), NO (ppm mixture in N₂) (Messer Griesheim) and NO₂ (99.5%) (Merck). A mixture of 15% O₃ diluted in O₂ was taken from a laboratory ozone generator (Sander 301.19). Both cis, trans- and trans, transhexa-2,4-dienedial were made by rearrangement (thermolysis and triethylamine catalysis, respectively) of *cis,cis*-hexa-2,4dienedial which was synthesized by NaIO₄ oxidation of ciscyclohexadiene-1,2-diole (Fluka).¹⁹ cis-Butenedial²⁰ was synthesized by reacting furan (>99%) with dimethyldioxirane.²¹ Benzene (>99.9%), phenol (>99.99%), nitrobenzene (99%), furan (>99%) (Aldrich) and p-benzoquinone (99.5%) (Fluka) were used as purchased. Formic acid (98%) (Fluka) was dried $(CuSO_4)$ just before use. Glyoxal monomer was prepared as described by Schweitzer et al.22 The purity of the organics was checked by GC-MS. The only detectable organic impurity of benzene was methylcyclohexane (<0.01%).

Results and discussion

OH/benzene adduct + O₂ (NO)

Experiments at 100 mbar. The first set of experiments was performed at a total pressure of 100 mbar with an O₂ concentration of 1.2×10^{18} molecule cm⁻³. The initial benzene concentration was 3.8×10^{15} molecule cm⁻³ and 0.16-0.19% were converted. Added NO, $1.4-24.4 \times 10^{13}$ molecule cm⁻³, was needed for the OH formation via pathway (8) as well as to reduce peroxyl radicals to the corresponding oxyl radicals. The reaction of NO with the OH/benzene adduct radical was assumed to be negligible, $k_{\rm NO+adduct} < 10^{-14} \text{ cm}^3 \text{ molecule}^{-1}$ $s^{-1.6}$ The initial NO₂ concentration was measured to be $< 2 \times 10^{11}$ molecule cm⁻³ by means of FT-IR spectroscopy.

In Fig. 2 a typical total ion chromatogram from a GC-MS analysis is shown, initial [NO] = 2.44×10^{14} molecule cm⁻³ and $\Delta[C_6H_6] = 7.2 \times 10^{12}$ molecule cm⁻³. Besides small impurities in the system, p-benzoquinone, phenol, isomers of hexa-2,4-dienedial and nitrobenzene were identified. The shape of the p-benzoquinone peak points to effective wall interactions or, probably, the formation of this substance in the heated sample loop or in the GC column. Because of nearly identical retention times for cis, cis- and cis, trans-hexa-2, 4-dienedial, only the sum of both substances was detected. In the FT-IR spectra, product bands arising from NO₂, pbenzoquinone, phenol, hexa-2,4-dienedial and nitrobenzene were visible. The main component of the hexa-2,4-dienedials was the trans, trans-species identified by means of the characteristic absorption at 1088 cm⁻¹, cf. Fig. 3. After subtraction of the reference spectrum of trans, trans-hexa-2,4-dienedial, the residual absorptions in the range 1700-1720 cm⁻¹ were found to be small. As a result of all experiments of this series, trans, trans-hexa-2,4-dienedial accounted for approximately 90% of the carbonyl absorption in this range. On the other hand, the results of the GC-MS analysis, cf. Fig. 2, suggested a higher fraction of cis.cis- and cis.trans-hexa-2,4-dienedial in the overall yield of the hexa-2,4-dienedials (for the isomers a nearly equal ion yield in the MS is expected). A possible reason for this discrepancy is different wall interactions of these polar substances using this GC-MS technique, including the sampling. Fig. 4 shows the formation yields of NO_2 , phenol, trans, trans-hexa-2, 4-dienedial and nitrobenzene in dependence on the initial NO concentration normalised by the amount of reacted benzene. p-Benzoquinone (not given in the figure) was found to be independent of the NO concentration with a yield of 0.08 ± 0.02 . The yield of NO₂ increased

0 10 12 14 16 retention time / min Fig. 2 Typical total ion chromatogram from a GC-MS analysis obtained for the reaction of the OH/benzene adduct with O2 in the

presence of NO, (100 mbar, 295 K).





Fig. 3 Reference FT-IR spectra of *trans,trans-*, *cis,trans-* and *cis,cis*-hexa-2,4-dienedial.

with increasing NO from a value of 1 to approximately 2. For each produced OH radical (and hence for each reacted C_6H_6) one molecule of NO₂ was formed *via* pathway (8). Additionally formed NO₂ can be explained with a reaction of



Fig. 4 Obtained product yields for the reaction of the OH/benzene adduct with O_2 in dependence on added NO, (100 mbar, 295 K).

peroxyl radicals with NO, which becomes more important with increasing NO concentration in the gas mixture.

$$RO_2 + NO \rightarrow RO + NO_2, \quad R \neq H$$
 (11)

With increasing NO there was also a clear increase in the formation yield of *trans,trans*-hexa-2,4-dienedial. This suggests that, *via* the generalised pathway (11), the precursor for the *trans,trans*-hexa-2,4-dienedial was formed, namely the 2hydroxycyclohexadienyloxyl radical.

$$\overset{OH}{\longleftarrow} \overset{OH}{\longrightarrow} \overset{OH}{\longrightarrow} \overset{OH}{\longleftarrow} \overset{OH}{\longrightarrow} \overset{(12)}{\longleftarrow} \overset{(12)}{\longleftarrow} \overset{(12)}{\longleftarrow} \overset{(12)}{\longleftarrow} \overset{(12)}{\longleftarrow} \overset{(12)}{\longleftarrow} \overset{(12)}{\longrightarrow} \overset{(12)}$$

Starting from the 2-hydroxycyclohexadienyloxyl radical, for the formation of *trans,trans*-2,4-hexadienedial the following reaction sequence can be proposed, *cf.* Scheme 1: (1) A ring opening *via* β -scission takes place, forming a 6-hydroxy-1-oxohexa-2,4-dienyl radical that is initially in the *cis,cis*-form. This allyl-type radical can be stabilised to a *cis,trans*- or the *trans,trans*-form (only the *trans,trans*-species is shown in Scheme 1). (2) After abstraction of the hydroxy H-atom by O₂, hexa-2,4-dienedial is formed finally.

The increase in the NO₂ yield exceeded the increase in the yield of *trans,trans*-hexa-2,4-dienedial, indicating the occurrence of other peroxyl radicals reacting *via* pathway (11). Furthermore, with increasing NO₂ concentration in the gas mixture, the reaction of NO₂ with the OH/benzene adduct also became more important forming, finally, nitrobenzene and probably other products.¹²

$$\overset{OH}{\longmapsto} \overset{OH}{\longleftarrow} + NO_2 \longrightarrow \overset{NO_2}{\longmapsto} + H_2O(+ \text{ other products})$$
 (13)

For $[NO]/\Delta[C_6H_6] > 10$ $([NO] > 7 \times 10^{13}$ molecule cm⁻³) averaged yields for *trans,trans*-hexa-2,4-dienedial of 0.36 ± 0.02 and for nitrobenzene of 0.11 ± 0.02 were measured. The observed phenol yield decreased from 0.2 at the lowest NO concentration to 0.12 for the highest NO concentration, *cf*. Fig. 4. From the measured yields it was not clear whether the phenol yield was nearly constant for $[NO]/\Delta[C_6H_6] < 16$ ($[NO] < 10^{14}$ molecule cm⁻³) and decreased then for higher NO concentration or if there was a continuous decrease as depicted by the line in Fig. 4. A phenol yield of 0.2 is in agreement with a series of literature data (0.236 \pm 0.044,¹² 0.26 \pm 0.05¹³ and 0.23 \pm 0.07¹⁰) but in contradiction to a yield of 0.50 \pm 0.05¹⁴ reported from a large chamber. It is to be noted that in the previously described experiments of the present study the initial $[NO]/[O_2]$ ratio



was in the range of $1.2-20 \times 10^{-5}$, which is at least two orders of magnitude higher compared to atmospheric conditions ([NO]/[O₂] = $5-10 \times 10^{-8}$ for 10–20 ppb NO). From the dependence of the phenol yield on the NO concentration given in Fig. 4 a further increase of the phenol yield for decreasing NO could not be ruled out. From a mechanistic point of view, the formation of phenol can be explained by H-atom abstraction by O₂ on the C-atom with the OH group *via* (4a)

$$\overset{OH}{\longleftarrow} \overset{OH}{\longleftarrow} \overset{OH}{\longleftarrow} \overset{OH}{\longleftarrow} \overset{OH}{\longleftarrow}$$

or by an intramolecular H-atom abstraction by the peroxyl group of the 2-hydroxycyclohexadienylperoxyl radical and subsequent β -scission²³ (as shown in (5a)).

$$\overset{\text{OH}}{\longmapsto} \overset{\text{OH}}{\longrightarrow} \overset{\text{OH}}{\longmapsto} \overset{\text{OH}}{\longrightarrow} \overset{\text{OH}}{\longrightarrow} \overset{\text{OH}}{\longmapsto} \overset{\text{OH}}{\longmapsto} \tag{5a}$$

Experiments at 500 mbar. The experiments were performed in the temperature range 276–353 K using the following initial concentrations (calculated for 298 K): $[O_2] = 8 \times 10^{18}$ molecule cm⁻³, $[C_6H_6] = 2.75 \times 10^{15}$ molecule cm⁻³ (conversion: 0.084–0.34%), $[NO] = 8.1–163 \times 10^{12}$ molecule cm⁻³. In these experiments the initial ratio $[NO]/[O_2]$ was in the range $1-20 \times 10^{-6}$, which is one order of magnitude lower compared to the experiments at 100 mbar.

In accordance with the experimental findings of the 100 mbar experiments, from GC-MS runs the formation of pbenzoquinone, phenol and nitrobenzene was observed. For the highest $[NO]/[O_2]$ ratios there was also experimental evidence for the formation of hexa-2,4-dienedials. As expected from the NO_x dependence of the nitrobenzene yield, cf. Fig. 4, with decreasing [NO]/[O₂] ratio (and also decreasing $[NO_x]/[O_2]$ ratio) the peak intensity of nitrobenzene decreased. However, even for the lowest [NO]/[O2] ratio nitrobenzene was detectable by means of GC-MS. In the upper part of Fig. 5 a typical difference FT-IR spectrum is plotted; T = 311 K, initial [NO] = 8.1×10^{12} molecule cm⁻³ and Δ [C₆H₆] = 3.8×10^{12} molecule cm⁻³. In the recorded difference spectra (H-atom formation was switched off or on) consumed reactants appear as negative absorptions and the products as positive absorptions. Beside the absorption of NO_2 and the negative bands arising from reacted benzene and NO, phenol (1183, 1261, 1507 and 3650 cm⁻¹) and unidentified carbonylic substances (1714 and 1737 cm^{-1}) were detected as the products. Especially in the experiments at the lower temperatures, for high [NO]/[O₂] ratios a small band located at 1088 cm⁻¹ appeared. This absorption was attributed to trans, trans-hexa-2, 4-dienedial, cf. Fig. 3, in accordance with the NO dependence of the formation yield of trans, transhexa-2,4-dienedial discussed in the previous section. After spectral subtraction of phenol from the primary spectrum, besides NO only product absorptions of carbonylic substances at 1714 and 1737 cm⁻¹ remained, cf. lower part of Fig. 5. The chemical structure of these substances is not clear. In Fig. 6 the reference spectra of *cis*-butenedial $(2.7 \times 10^{12} \text{ mol-}$ ecule cm⁻³) and glyoxal (4.5×10^{12} molecule cm⁻³) are given. These substances (or the alkyl substituted analogous species) are frequently discussed as products of the reaction of OH radicals with aromatics under atmospheric conditions.^{1,8} The



Fig. 5 FT-IR product spectrum obtained for the reaction of the OH/ benzene adduct with O_2 in the presence of NO before (upper part) and after phenol subtraction (lower part), (500 mbar, 311 K); phenol (1183, 1261, 1507 and 3650 cm⁻¹), unidentified carbonylic substances (1714 and 1737 cm⁻¹).

position of the product band centred at 1714 cm^{-1} indicates that *cis*-butenedial and glyoxal were not the main carbonylic products. Nevertheless, from the FT-IR measurements the formation of *cis*-butenedial and glyoxal could not totally be



Fig. 6 Reference FT-IR spectra of *cis*-butenedial $(2.7 \times 10^{12} \text{ mol-ecule cm}^{-3})$ and glyoxal $(4.5 \times 10^{12} \text{ molecule cm}^{-3})$.

ruled out. Additional experiments were carried out using a derivatisation technique for carbonylic substances, see below. For the other substances detected by GC-MS analysis, pbenzoquinone and nitrobenzene, the intensities of the FT-IR absorptions in most cases were too small, making a quantitative determination impossible.

Fig. 7 shows the obtained phenol yields at four temperatures in dependence on the initial $[NO]/[O_2]$ ratio. The curves in Fig. 7 are results from modeling and will be discussed later. Two different flow tubes were used with a change in the surface/volume ratio by a factor of 5 (inner diameter: 1.8 or 4.0 cm). The absence of significant differences in the product yields suggested an absence of noticeable wall reactions. Generally, for a fixed temperature a clear increase of the phenol yield for decreasing NO concentrations (decreasing initial [NO]/[O₂] ratio) was observed. And for a fixed initial $[NO]/[O_2]$ ratio, there was a distinct increase of the phenol yield with increasing temperature, cf. Table 1. The total yield of the carbonylic substances (obtained from the integrated band intensity in the range 1690-1780 cm⁻¹) showed an inverse behaviour with respect to the phenol yield. The yield of the carbonylic substances increased with both increasing NO concentrations and decreasing temperature. This is



Fig. 7 Measured phenol yields in dependence on the initial [NO]/[O₂] ratio for four temperatures, (500 mbar, 276–353 K). Plotted curves arise from modeling (see text), full line using ΔH_3 = $-47.5 \text{ kJ mol}^{-123}$ and dotted line using $\Delta H_3 = -4.6 \text{ kJ mol}^{-1.6}$

Table 1 Measured product yields at p = 500 mbar and initial $[NO]/[O_2] = 1 - 1.5 \times 10^{-6}$

<i>T/</i> K	Phenol	Carbonyl ^a (total)	Glyoxal (upper limit)	Furan
353 311 293 276	$\begin{array}{c} 0.68 \pm 0.05 \\ 0.45 \pm 0.06 \\ 0.30 \pm 0.02 \\ 0.18 \pm 0.04 \end{array}$	$\begin{array}{c} 0.29 \pm 0.04 \\ 0.42 \pm 0.04 \\ 0.59 \pm 0.02 \\ 0.64 \pm 0.09 \end{array}$	n.d. 0.32 ± 0.04 0.22 ± 0.02 0.18 ± 0.04	n.d. n.d. 0.017 ± 0.011 n.d.

^a Obtained from the integrated band intensity in the range 1690-1780 cm⁻¹. n.d. not determined.



Fig. 8 Measured formation yields of phenol and carbonylic substances (total amount) in dependence on the initial [NO]/[O₂] ratio, (500 mbar, 276 and 353 K).

demonstrated in Fig. 8 for the highest and lowest temperature investigated.

Identification of glyoxal, cis-butenedial and furan. To identify the carbonylic substances still unknown, additional experiments have been performed using the PFBHA derivatisation technique.¹⁷ Under commonly used experimental conditions (initial $[NO]/[O_2] = 1.5 \times 10^{-6}$) reaction products were trapped at liquid argon temperature for 45-180 min. Besides the background impurities, the only detected oximes were those formed from glyoxal. There were no indications for the occurrence of oximes arising from cis-butenedial or other reaction products.

Because glyoxal was identified as a reaction product by means of the derivatisation technique, it was assumed that glyoxal was involved in the carbonyl absorption measured by FT-IR, cf. the left shoulder of the carbonyl absorption in Fig. 5 and the reference spectrum in Fig. 6. Upper limits of the glyoxal formation yield were obtained by spectral subtraction of a calibrated reference spectrum from the measured product spectra, cf. Table 1. Because of the low signal intensity of the carbonyl absorption in the range around 1740 cm⁻¹ at 353 K a reasonable determination of the glyoxal yield was impossible. It is to be noted that the left shoulder of the carbonyl absorption in the product FT-IR spectra can also be due to other compounds, at least partly. Therefore, the given glyoxal yields represent only upper limits and the actual yields can be much lower.

Furthermore, in experiments with on-line GC-MS analysis, cis-butenedial was introduced into the flow tube on the port for the C₆H₆ entrance. Using this analytical technique, cisbutenedial was found to be detectable with a sufficient efficiency and a detection limit of approximately 1×10^{11} molecule cm^{-3} was found. In all GC-MS chromatograms the peak of cis-butenedial was below the detection limit. With an amount of reacted C_6H_6 in the range of 2.3–9.4 × 10¹² molecule cm⁻³ a *cis*-butenedial formation yield of <0.04 follows.

Because there was no experimental hint for the occurrence of *cis*-butenedial, an effort was undertaken to identify other possible C₄-co-products of glyoxal (C₂). By means of GC-MS analysis (column: Poraplot Q) furan was detected as a reaction product using the ion trace at m/z = 68. Concentrations of formed furan were determined at 293 K for an initial [NO]/[O₂] = 1.5×10^{-6} . From the simultaneously measured amount of reacted C₆H₆ by FT-IR, the formation yield of furan was found to be 0.017 ± 0.011. Because of the small furan yield, no further experiments by variation of the conditions were performed.

Mechanism and modeling. In Scheme 2 the possible pathways for the formation of phenol, the carbonylic substances and possibly other products (labelled "products") are summarised together with formation pathways of hexa-2,4-dienedial and nitrobenzene which might be important in the presence of a sufficient amount of NO_x . Because of the lack of mechanistic information concerning the formation of glyoxal and furan, both substances were not explicitly presented in Scheme 2. Glyoxal and furan are thus included in "products".

It is to be noted that the scheme is nearly identical with that proposed by Bohn and Zetzsch.⁷ For a more detailed description of the product formation, the original pathways (4) and (5) were each split into the sub-pathways (a) for phenol formation and the sub-pathways (b) for the formation of "products". Using Scheme 2 an attempt was undertaken to describe the temperature- and NO_x-dependence of the obtained phenol yields, *cf.* Fig. 7. With $K_3 = k_3/k_{-3}$ the experimentally observed rate constant for the overall decay of the OH/benzene adduct in the reaction with O₂ in the absence of NO_x^{-6,7} is given as:

$$k_{\text{overall}} = k_{4a} + k_{4b} + K_3(k_{5a} + k_{5b}) \tag{I}$$

Defining $k_{\text{phenol}} = k_{4a} + K_3 k_{5a}$ and $k_{\text{products}} = k_{4b} + K_3 k_{5b}$ the phenol yield is expressed according to the pathways considered in Scheme 2 by:

$$Y_{\rm phenol} = \frac{k_{\rm phenol}}{k_{\rm overall} + K_3 k_{12} [\rm NO] + k_{13} [\rm NO_2] / [\rm O_2]} \quad (\rm II)$$

With the measured $k_{overall}$ data from the literature (in units of 10^{-16} cm³ molecule⁻¹ s⁻¹; 1.6 \pm 0.6 (299 K), 2.1 \pm 0.4 (314 K), 3.0 \pm 0.3 (333 K) and 3.7 \pm 0.4 (354 K))²⁴ the following Arrhenius expression can be derived, *cf.* Fig. 9:

$$k_{\text{overall}} = 4.0 \times 10^{-14} \exp\left(\frac{-1649}{T}\right) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$
(III)

For the equilibrium constant K_3 only one experimentally obtained value exists in the literature, $K_3 = 2.7 \pm 0.4 \times 10^{-19}$ cm³ molecule⁻¹ for T = 297 K.⁷ To describe the temperature



Scheme 2

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Fig. 9 Arrhenius plots for $k_{overall}$ using data from ref. 24 and for the derived data of k_{phenol} and $k_{products}$ from the modeling (see text).

dependence of K_3 , the needed reaction enthalpy change ΔH_3 is proposed from theoretical studies to be $-47.5 \text{ kJ mol}^{-123}$ and $-4.6 \text{ kJ mol}^{-1.9}$ Neglecting the temperature dependence of the enthalpy change, K_3 can be given as follows:

$$K_3 = 1.2 \times 10^{-27} \exp\left(\frac{5713}{T}\right) \text{ cm}^3 \text{ molecule}^{-1}$$

 $(\Delta H_3 \text{ from ref. 23})$ (IV)

$$K_3 = 4.2 \times 10^{-20} \exp\left(\frac{553}{T}\right) \text{ cm}^3 \text{ molecule}^{-1}$$

 $(\Delta H_3 \text{ from ref. 9})$ (V)

The rate constant for the reaction of the 2hydroxycyclohexadienylperoxyl radical with NO, $k_{12} = 1.1 \pm 0.4 \times 10^{-11}$ cm³ molecule⁻¹ s^{-1,7} measured at T = 297 K was used for the whole temperature range. The Arrhenius activation energies for RO₂ + NO (R = CH₃, C₂H₅ and *n*-C₃H₇) have been found to be -(1-3) kJ mol^{-1.25,26} By analogy, the temperature dependence of k_{12} was assumed to be of minor importance in the considered range of 276–353 K. For k_{13} a temperature independent value of 2.5×10^{-11} cm³ molecule⁻¹ s⁻¹ was used, derived from measurements in the temperature range 305–349 K.⁶

For initial [NO]/[O₂] = $1-1.2 \times 10^{-6}$ and $Y_{\text{phenol}} = 0.18$ (276 K), 0.30 (293 K), 0.45 (311 K) and 0.68 (353 K) from Fig. 7, k_{phenol} was calculated from the rearranged eqn. (II) for both values of the reaction enthalpy change using eqns. (III)–(V). Under the considered experimental conditions, NO was consumed in considerable amounts mainly by pathway (8). Therefore, the initial NO concentration was not appropriate for eqn. (II) and an averaged amount of consumed NO (and also of produced NO₂) of 3.5×10^{12} molecule cm⁻³ (calculated for 298 K) was taken into account. Table 2 summarises k_{phenol} and $k_{\text{products}} = k_{\text{overall}} - k_{\text{phenol}}$ in dependence on temperature for both values of the reaction enthalpy change. The corresponding Arrhenius plots, including the plot of k_{overall} (eqn. (III)) are given in Fig. 9; full symbols and full line: data

Table 2 Calculated k_{phenol} and k_{products} for different values of ΔH_3 (see text)

T/ K	Y_{phenol}	$k_{\text{phenol}}{}^{a/}$ cm ³ molecule ⁻¹ s ⁻¹	$k_{\text{products}}^{a/}$ cm ³ molecule ⁻¹ s ⁻¹	$k_{\text{phenol}}{}^{b}/$ cm ³ molecule ⁻¹ s ⁻¹	$k_{\text{products}}^{b/}$ cm ³ molecule ⁻¹ s ⁻¹
353 311 293 276	0.68 0.45 0.30 0.18	$\begin{array}{c} 2.64 \times 10^{-16} \\ 9.76 \times 10^{-17} \\ 5.20 \times 10^{-17} \\ 3.16 \times 10^{-17} \end{array}$	$\begin{array}{c} 1.13 \times 10^{-16} \\ 1.03 \times 10^{-16} \\ 9.28 \times 10^{-17} \\ 7.08 \times 10^{-17} \end{array}$	$\begin{array}{c} 2.70 \times 10^{-16} \\ 1.00 \times 10^{-16} \\ 5.09 \times 10^{-17} \\ 2.34 \times 10^{-17} \end{array}$	$\begin{array}{c} 1.08 \times 10^{-16} \\ 1.00 \times 10^{-16} \\ 9.40 \times 10^{-17} \\ 7.90 \times 10^{-17} \end{array}$
$^{a}\Delta H_{3} = -$	$-47.5 \text{ kJ mol}^{-1}$	from ref. 23. ^{<i>b</i>} $\Delta H_3 = -4.6 \text{ kJ}$	mol^{-1} from ref. 9.		

obtained using $\Delta H_3 = -47.5$ kJ mol⁻¹²³ and open symbols and dotted line: data obtained using -4.6 kJ mol^{-1.9}

The data for k_{phenol} show a reasonable linearity and the following Arrhenius expressions can be given:

$$k_{\text{phenol}} = 5.8 \times 10^{-13} \exp\left(\frac{-2719}{T}\right) \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

($\Delta H_3 \text{ from ref. 23}$) (VI)

$$k_{\text{phenol}} = 1.7 \times 10^{-12} \exp\left(\frac{-3072}{T}\right) \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

 $(\Delta H_3 \text{ from ref. 9})$ (VII)

Assuming that pathway (4a) is dominant for phenol formation, the Arrhenius activation energy of 23-26 kJ mol⁻¹ from eqns. (VI) and (VII) stands for an H-atom abstraction by O_2 . For example, the Arrhenius activation energy for the reaction of $CH_3O + O_2 \rightarrow CH_2O + HO_2$ was found to be 11–20 kJ mol^{-127–29} and, also, the pre-exponential factors were of the same order of magnitude. This indicates that the observed temperature dependence of phenol formation is not in contradiction with a phenol formation via pathway (4a). On the other hand, if pathway (5a) is dominant the Arrhenius activation energy for this pathway should be 70 kJ mol⁻¹ ($\Delta H_3 = -47.5$ kJ mol^{-1 23}) or 30 kJ mol⁻¹ ($\Delta H_3 = -4.6$ kJ mol⁻¹⁹). From the given $(T/K)^n$ -dependence from a theoretical study,²³ an Arrhenius activation energy for pathway (5a) of 53 kJ mol^{-1} can be estimated. The agreement with either of the two derived values of 70 and 30 kJ mol⁻¹ is unsatisfactory. Nevertheless, taking into account a probably high inaccuracy of ΔH_3 , from these considerations the formation of phenol via pathway (5a) can not be ruled out. The data for k_{products} in Fig. 9 are slightly curved and indicate a relatively small or negligible temperature dependence for this process. If pathway (4b) is dominant for the formation of the "products" (carbonylic substances and others), pathway (4b) should be a nearly barrier free process. However, for the reaction of a radical with O₂ with a rate constant of 10^{-16} cm³ molecule⁻¹ s⁻¹ at room temperature, the existence of a significant barrier has to be expected. Therefore, it is more likely that pathway (5b) represents the predominant pathway for the formation of the "products". For $\Delta H_3 = -4.6 \text{ kJ mol}^{-19}$ or $\Delta H_3 = -47.5 \text{ kJ}$ mol⁻¹²³ Arrhenius activation energies for pathway (5b) of 5 kJ mol⁻¹ or 48 kJ mol⁻¹ follow. The latter is more appropriate for a unimolecular reaction of a radical.³⁰ Tentatively, this fact can be taken as an argument to favour the value of $\Delta H_3 = -47.5 \text{ kJ mol}^{-1.23}$

Besides the uncertainty in the description of the temperature dependence of the equilibrium constant K_3 , a critical point for the modeling is the availability of $k_{overall}$ data and the extrapolation of experimental values to lower temperatures, cf. Fig. 9. The curvature in the data for $k_{products}$ is probably caused by the inaccurate description of $k_{overall}$ at lower temperatures. Nevertheless, the calculated phenol yields from eqn. (II) for $\Delta H_3 = -47.5$ kJ mol⁻¹²³ using eqn. (IV) and eqn. (VI) (full line) and for $\Delta H_3 = -4.6$ kJ mol⁻¹⁹ using eqn. (V) and eqn. (VII) (dotted line) are in reasonable agreement with the experimental data, cf. Fig. 7. This indicates that in Scheme 2, and with the help of the corresponding Arrhenius expressions, the main processes are well described.

$OH/benzene adduct + O_3$

In addition, experiments have been performed under conditions of a preferred reaction of the OH/benzene adduct with O_3 . In the gas-phase mechanism RACM,³¹ the reaction of the OH/benzene adduct with O_3 is considered to be in competition with the reactions of the OH/benzene adduct with O_2 and NO_2 . This is pointed out for the model species toluene, xylene and cresol and the proposed reaction pathway can be given in the generalised form shown in pathway (14) (here for benzene).

$$\overset{OH}{\longrightarrow} \overset{OH}{\longleftarrow} \overset{OH}{\longrightarrow} \overset{OH}{\longrightarrow} \overset{OH}{\longleftarrow}$$
(14)

In the original work³¹ pathway (14) was used to explain discrepancies in the yields of phenol-type compounds arising from different chamber experiments.

The experiments have been performed at a total pressure of 100 mbar with initial O_3 concentrations in the range 1.1– 5.6 × 10¹⁴ molecule cm⁻³ using a mixture of 15% O_3 diluted in O_2 . The carrier gas was He. The initial benzene concentration was 3.8×10^{15} molecule cm⁻³ and 0.17–0.38% of the benzene were converted. In the literature, rate constants for the reaction of O_3 with small alkyl radicals are of the order of 10^{-12} – 10^{-11} cm³ molecule⁻¹ s⁻¹²⁶ which is 4–5 orders of magnitude higher compared with the rate constant for the overall reaction of O_2 with the OH/benzene adduct.⁶ Therefore, under the present conditions a contribution of the O_2 reaction was negligible.

For qualitative analysis, in GC-MS runs the formation of p-benzoquinone, trans, trans-hexa-2, 4-dienedial and phenol were identified by means of the retention time and the mass spectrum of authentic samples. Fig. 10 shows a typical result of a FT-IR measurement, $[O_3] = 5.4 \times 10^{14}$ molecule cm⁻³ and $\Delta [C_6 H_6] = 7.1 \times 10^{12}$ molecule cm⁻³. In accordance with GC-MS analysis, bands arising from trans, trans-hexa-2,4dienedial (1088, 1714, 2726 and partly 2819 cm^{-1}) and phenol (1183, 1261, 1507, 1605 and 3650 cm⁻¹) were observed. For comparison, in Fig. 3 the FT-IR reference spectrum of trans, trans-hexa-2, 4-dienedial together with the spectra of the cis,trans- and the cis,cis-isomer are given. Furthermore, bands located at 1118 and 1791 cm⁻¹ and in overlapping with other absorptions at 1759 cm⁻¹ were attributed to formic acid. After spectral subtraction of the identified products, there were remaining absorptions in the carbonyl absorption range 1700-1750 cm⁻¹, indicating the occurrence of further unidentified carbonylic substances. The expected absorption of *p*-benzoquinone centred at 1680 cm^{-1} was not clearly visible in this series of experiments. This is probably caused by the very strong carbonyl absorption of trans, trans-hexa-2,4dienedial in this region, and, on the other hand, the relatively low formation yield of p-benzoquinone. The bands located at



Fig. 10 FT-IR product spectrum obtained for the reaction of the OH/benzene adduct with O_3 , (100 mbar, 295 K); *trans,trans-hexa-2,4-*dienedial (1088, 1714, 2726 and partly 2819 cm⁻¹), phenol (1183, 1261, 1507, 1605 and 3650 cm⁻¹), formic acid (1118 and 1791 cm⁻¹).

2123 and 2172 cm⁻¹ were attributed to CO (in the sample spectrum of Fig. 10 the first band is overlapped by the absorption of reacted O_3). Because of the relatively small signal intensity for CO and the influence of O_3 absorption, a determination of the CO concentration was not carried out. As a result of FT-IR analysis, Fig. 11 shows the detected product yields for *trans,trans*-hexa-2,4-dienedial, phenol and formic acid. The yields are plotted in dependence on the initial ozone



Fig. 11 Obtained product yields for the reaction of the OH/benzene adduct with O_3 in dependence on added O_3 , (100 mbar, 295 K).



Scheme 3

concentration normalised by the amount of reacted benzene. The yields of trans, trans-hexa-2, 4-dienedial and formic acid increased with increasing O₃ concentration, resulting, for $[O_3]/\Delta[C_6H_6] > 30$, in maximum values of 0.28 ± 0.02 and $0.12\pm0.02,$ respectively. This behaviour can be explained by a more effective reaction of O3 with the OH/benzene adduct with increasing O_3 concentration in competition with the selfreaction of the OH/benzene adduct or the reaction with other species, cf. Scheme 3. Starting from the 2-hydroxycyclohexadienyloxyl radical, analogous to the reaction sequence from Scheme 1, the formation of trans, trans-hexa-2, 4-dienedial can be described. It is to be noted that in the GC runs no indications for the occurrence of cis, cis- and cis, trans-hexa-2,4-dienedial were found, indicating a favoured conversion of the original cis, cis-form of the cyclic radicals into the trans, transform after ring opening. For the other reaction products of Scheme 3 (formic acid, CO and the unidentified carbonylic substances) a reasoned formation mechanism can not be specified.

The observed phenol yield (0.20 ± 0.05) was afflicted with a relatively large degree of scatter and no dependence of the yield on experimental conditions was visible, *cf.* Fig. 11. Therefore, it is not clear whether O₃ was involved in the process of phenol formation. Thus it seems to be highly speculative to point out a formation mechanism for phenol under these experimental conditions. Generally, the experimental findings of this study do not support pathway (14) as the dominant reaction of O₃ with the OH/benzene adduct radical.

Summary and application to the atmosphere

Under conditions of a predominant reaction of the OH/ benzene adduct with O₂ the product formation was investigated in dependence on the NO concentration. Products were the isomers of hexa-2,4-dienedial, phenol, nitrobenzene, pbenzoquinone, glyoxal, furan and unidentified carbonylic substances. In experiments with high [NO]/[O2] ratios, with increasing NO concentrations the yields of trans, trans-hexa-2, 4-dienedial and nitrobenzene increased resulting in maximum values of 0.36 ± 0.02 and 0.11 ± 0.02 , respectively, for $[NO]/\Delta[C_6H_6] > 10$ (100 mbar, 295 K). In experiments with relatively low [NO]/[O₂] ratios the phenol yield was determined in dependence on temperature and NO concentration (500 mbar, 276-353 K). Under these experimental conditions, in most cases the concentrations of trans, trans-hexa-2,4-dienedial, nitrobenzene and p-benzoquinone were below the detection limit (FT-IR analysis). The phenol yield increased with increasing temperature and decreasing NO concentrations. The total yield of carbonylic substances showed an inverse behaviour with respect to the phenol yield. Table 1 summarises the obtained product yields for initial $[NO]/[O_2] = 1-1.2 \times 10^{-6}$. Generally, the phenol yield and the whole product distribution was found to noticeably depend on the experimental conditions. Therefore, differences in the reported phenol yields $(0.236 \pm 0.044)^{12}$ $0.26 \pm 0.05)^{13}$ 0.50 ± 0.05^{14} and 0.23 ± 0.07^{10}) can, at least partly, be explained by different experimental conditions. In the liter-

Table 3 Expressions of the formation yield for the different productsderived from Scheme 2

Product	Yield
Phenol	$\frac{k_{\text{phenol}}}{k_{\text{max}} + K_2 k_{12} [\text{NO}_2] / [\text{O}_2]}$
Products ^a	$\frac{k_{\text{overall}} - k_{\text{phenol}}}{k_{\text{overall}} - k_{\text{phenol}}}$
Hexa-2,4-dienedial	$\frac{K_{\text{overall}} + K_3 k_{12} [10] + k_{13} [10] k_{12} [10]}{K_3 k_{12} [NO]}$
Nitrobenzene ^b	$\frac{k_{\text{overall}} + K_3 k_{12} [\text{NO}] + k_{13} [\text{NO}_2] / [\text{O}_2]}{k_{13} [\text{NO}_2] / [\text{O}_2]}$
^a Unidentified carbonylic	$k_{\text{overall}} + K_3 k_{12} [\text{NO}] + k_{13} [\text{NO}_2] / [\text{O}_2]$ substances and others. ^b An upper limit is

" Unidentified carbonylic substances and others. " An upper limit is given, see text.

ature a glyoxal yield of 0.207 ± 0.019^{11} (298 ± 2 K) is reported as a result of a chamber study using NO_x concentrations in the range of 10^{14} molecule cm⁻³. The upper limits of the glyoxal yields from the present study, 0.22 ± 0.02 (293 K) and 0.32 ± 0.04 (311 K), measured for lower NO_x concentrations are not in contradiction with the result of the chamber study.

A reaction scheme is proposed describing the formation of phenol, nitrobenzene (upper limit), the hexa-2,4-dienedials and other products (unidentified carbonylic substances *etc.*). This scheme is in accordance with a previously published mechanism⁷ and was used for the modeling of the experimental findings. Using a series of kinetic data from the literature^{6,7,24} the rate constants for the formation of phenol and the formation of "products" (carbonylic substances and others) were estimated for two different reaction enthalpy changes ΔH_3 .^{9,23} The model allows to predict formation yields of the different products in dependence on temperature and NO_x concentration. Table 3 summarizes the expressions



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for the formation yields, *cf.* Scheme 2. The corresponding kinetic parameters are given in Table 4 assuming the two reaction enthalpy changes ΔH_3 from the literature.^{9,23} For instance, for an urban area at T = 295 K and mixing ratios of 10 ppb for NO and 20 ppb for NO₂ the following yields can be predicted: $Y_{\text{phenol}} = 0.38$, $Y_{\text{products}} = 0.60$, $Y_{\text{hexa-2,4-dienedial}} = 0.0055$ and $Y_{\text{nitrobenzene}} \leq 0.016$. For this example the reaction enthalpy change $\Delta H_3 = -47.5$ kJ mol⁻¹²³ was assumed. Because, *via* pathway (13), other products than nitrobenzene yield can be given.

From the modeling there was an indication that pathway (5b) probably represents the predominant pathway for the formation of the "products" (carbonylic substances and others). Possible products of this unimolecular step may be an O₂bridged bicyclic allyl radical²³ or an epoxycyclohexen-oxyl radical,³² cf. Scheme 4. Assuming successive β-scissions, from the O₂-bridged bicyclic allyl radical the formation of glyoxal and furan can be explained. By analogy with the proposed pathways for the formation of hexa-2,4-dienedial from the 2hydroxycyclohexadienyloxyl radical, after ring opening via βscission of the epoxycyclohexenoxyl radical and subsequent abstraction of the hydroxy H-atom by O_2 the corresponding 2,3-epoxyhex-4-enedial can be formed, cf. Scheme 4. All efforts to synthesize this compound were without success. Because of the lack of clear experimental findings, the formation of the O₂-bridged bicyclic allyl radical²³ as well as the epoxycyclohexenoxyl radical³² remains speculative.

A product study concerning the reaction of the OH/benzene adduct with O₃ is reported for the first time. Products were *trans,trans*-hexa-2,4-dienedial, formic acid, phenol, *p*-benzoquinone, CO and unidentified carbonylic substances. With increasing O₃ concentrations the yields of *trans,trans*-hexa-2, 4-dienedial and formic acid increased, resulting in maximum values of 0.28 ± 0.02 and 0.12 ± 0.02 , respectively, for $[O_3]/\Delta[C_6H_6] > 30$ (100 mbar, 295 K). The observed phenol yield of 0.20 ± 0.05 was found without a clear dependence on the O₃ concentration. The experimental findings of this study do not support pathway (14) to be dominant for the reaction of the OH/benzene adduct with O₃ as proposed in the gasphase mechanism RACM.³¹

Generally, more experimental work is needed to extend our knowledge concerning the product distributions by variation of experimental conditions. From this, further improvement of the models describing the atmospheric degradation processes of aromatic compounds can be expected.

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	A or $K_{(T=\infty)}/$ cm ³ molecule ⁻¹ s ⁻¹ or cm ³ molecule ⁻¹	$E_{ m A}/R$ or $\Delta H/R/K$	Remarks
k _{overall} k _{phenol}	4.0×10^{-14} 5.8 × 10 ⁻¹³	1649 2719	Data from ref. 24 Using ΔH_3 from ref. 23
k ₁₂	1.7×10^{-12} 1.1×10^{-11}		Using ΔH_3 from ref. 9 Ref. 7, assumed to be <i>T</i> -independent
k ₁₃	2.5×10^{-11}	—	Ref. 6, assumed to be T -independent
<i>K</i> ₃	$\begin{array}{c} 1.2 \times 10^{-27} \\ 4.2 \times 10^{-20} \end{array}$	-5713 -553	ΔH_3 from ref. 23 ΔH_3 from ref. 9

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