Reactivity of OH radicals with chlorobenzoic acids—A pulse radiolysis and steady-state radiolysis study

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**Abstract**

The reactions of OH radicals with 2-, 3-, 4-chlorobenzoic acids (ClBzA) and chlorobenzene (ClBz), \(k(\rm{OH+substrate})=(4.5-6.2) \times 10^6 \, \text{dm}^3 \text{mol}^{-1} \, \text{s}^{-1}\), have been studied by pulse radiolysis in N\(_2\)O saturated solutions. The absorption maxima of the OH- adducts were in the range of 320–340 nm. Their decay was according to a second-order reaction, \(2k=(1-9) \times 10^6 \, \text{dm}^3 \text{mol}^{-1} \, \text{s}^{-1}\). In the presence of N\(_2\)O/O\(_2\) the formation of peroxyl radicals was detectable for 2-, 4-ClBzA and ClBz, \(k(\rm{OH-adduct+O}_2)=(2-4) \times 10^7 \, \text{dm}^3 \text{mol}^{-1} \, \text{s}^{-1}\), while this reaction for 3-ClBzA was too slow to be registered. In the presence of N\(_2\)O the degradation rates induced by gamma radiation were very similar for all chlorobenzoic acids, yet the chloride formation was distinctly higher for 3-ClBzA. In the presence of oxygen the initial degradation of 2- and 4-ClBzA equaled the OH-radical concentration, whereas in case of 3-ClBzA only ~65 of OH led to degradation. The order for the efficiency of dehalogenation was 4-\(2\)-3-ClBzA. Several primary radiolytic products could be detected by HPLC. To evaluate the toxicity of final products a bacterial bioluminescence test was carried out.

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1. Introduction

Chlorobenzoic acids, especially 4-ClBzA, were frequently used as model compounds to assess the efficiency of various oxidation technologies for degradation of chlorinated water pollutants e.g., photolysis and photocatalysis: D’Oliveira et al., 1993, Dionysiou et al., 2000, Han et al., 2004, Enriquez and Pichat, 2006; sonolysis and Fenton-like oxidations: Neppolian and Choi, 2001, Neppolian et al., 2004. Owing to the quantitative reaction of 4-ClBzA with OH radicals, it was used successfully in the last decade as a chemical probe for indirect measurement of OH-radical concentrations at the bench scale level (Han et al., 2002; Pi et al., 2005, Rosenfeldt et al., 2006). Up to now no comprehensive information on the reactions of OH radicals with 2-, 3- and 4-ClBzA had been given. In the present investigations ionizing radiation was applied to study the OH-radical induced processes of these substrates. The kinetic and spectroscopic data were achieved by pulse radiolysis, the rates for degradation, dechlorination and product formation were scrutinized by gamma-radiolysis and the results for the individual substances were compared. As known from previous reports concerning the reactions of \(e_{\text{aq}}\) with 2-, 3- and 4-ClBzA (Jankovic et al., 1998, Zona et al., 2008) the detected transients and the dechlorination rates were markedly dependent on the chlorine position. Since oxygen is consumed during irradiation, the effect of its concentration on the decomposition process was verified by using aerated and oxygenated solutions. To assess the water quality after irradiation of the ClBzA samples toxicity measurements were carried out.

2. Experimental section

2.1. Chemicals and abbreviations

Chlorobenzoic acids (2-ClBzA, 3-ClBzA, 4-ClBzA), chlorobenzene (ClBz), benzoic acid (BzA), 4-hydroxybenzoic acid (4-OHBzA), 4-chlorophenol (4-CIPhOH), 4-chloro-3-hydroxybenzoic acid (4-CI3OHBzA), 4-chloro-salicicylic acid (i.e. 4-chloro-2-hydroxybenzoic acid, 4-CI2OHBzA), 3-chloro-4-hydroxybenzoic acid (3-CI4OHBzA), 5-chloro-salicicylic acid (i.e. 5-chloro-2-hydroxybenzoic acid or 3-chloro-6-hydroxybenzoic acid, 3-Cl6OHBzA) and all other chemicals were purchased of highest purity grade available (Merck, Fluka, Sigma-Aldrich, Vienna, Austria) and used as supplied. The gases N\(_2\)O (Stickoxydul, p.n.) and O\(_2\) (purity grade 4,5) were from Messer Austria (Vienna, Austria). The solutions were freshly prepared before irradiation with triply distilled water and, when required, purged with the corresponding gases about 40 min. The pH was adjusted with NaOH. The concentrations of the used gases in aqueous solution at room temperature are: N\(_2\)O: \(2.8 \times 10^{-2} \, \text{mol dm}^{-3}\), O\(_2\): \(1.25 \times 10^{-3} \, \text{mol dm}^{-3}\).
2.2. Pulse radiolysis equipment

The 10 MeV Linac at Risø, (Haimson Research Corp., HRC-712), which provided pulses of 0.2–1 μs, was used (Sehested and Corfitzen, 1975). The detection system consisted of a 450 W xenon lamp, a quartz cell (light path 5.1 cm), a Perkin-Elmer double quartz prism monochromator and a photomultiplier IP28, equipped with a LeCroy digital oscilloscope, Model 9400, and an IBM PC/AT3 computer on line. The irradiation doses were 4–10 Gy per pulse. For determination of the absorbed dose a hexacyanoferrate(II) dosimeter, \( G(\text{OH}^+ + 	ext{e}_aq/\text{CO}) = 0.61 \text{μmol J}^{-1} \), \( \varepsilon_{420} = 1000 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1} \) (Schuler et al., 1981) was applied. The transients absorption spectra are presented in OD/cm normalized to a dose of 10 Gy. They represent mean values of at least three measurements. The experimental uncertainty of the given rate constants and extinction coefficients was about ± 10%.

2.3. Co-60-gamma-source

The steady-state irradiations were carried out with the “Gammacell 220” (Nordion International Inc., Kanata, ON, Canada) of the University of Vienna. The dose rate was 195 Gy min\(^{-1}\).

Fig. 1. Transient absorption spectra obtained in N\(_2\)O saturated aqueous solution of 2.5 × 10\(^{-4}\) mol dm\(^{-3}\) 2-chlorobenzoic acid, pH 10, (spectrum A, it includes about 10% of H-adduct absorption), and in N\(_2\)O/O\(_2\) (1:1) saturated solution after pulse (spectrum B1) and 400 ms after pulse (spectrum B2). OD/cm values are normalized to 10 Gy.

Fig. 2. Transient absorption spectra obtained in N\(_2\)O saturated aqueous solution of 5 × 10\(^{-4}\) mol dm\(^{-3}\) 3-chlorobenzoic acid, pH 10, (spectrum A, it includes about 10% of H-adduct absorption), and in N\(_2\)O/O\(_2\) (1:1) saturated solution after pulse (spectrum B1) and 400 μm after pulse (spectrum B2). OD/cm values are normalized to 10 Gy.
2.4. Product analysis

**HPLC-UV measurements**: The degradation of the monochlorobenzoic acids and the product formations were determined as a function of dose by reverse-phase liquid chromatography (Hewlett-Packard 1050/1100 series equipped with a quaternary pump (G1311A), a mobile phase degassing unit (G1322A), a diode array detector (series 1050), and an autosampler (D1311A) adapted with a 20 µL sample loop. Column: Spherisorb ODS 2 RP-18 (125 × 4 mm I.D., particle size: 5 µm) fitted with a guard column (4 × 4 mm I.D.) of the same material; temperature: 30 °C; injection volume: 20 µl; flow rate: 1 ml/min; eluent: H2O (0.1% w/v phosphoric acid)/CH3OH=60/40 v/v for 2-ClBzA and 4-ClBzA and H2O (0.1% w/v phosphoric acid)/CH3OH=50/50 v/v for 3-ClBzA. The detection wavelengths were 210, 235 and 280 nm. The identification of products was based on the conformance of their UV-spectra and retention times with reference compounds.

**Chloride analysis**: Chloride was determined spectrophotometrically at 460 nm (Lambda 650 UV/vis spectrophotometer, Perkin-

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**Fig. 3.** Transient absorption spectra obtained in N2O saturated aqueous solution of 2.5 × 10^{-4} mol dm^{-3} 4-chlorobenzoic acid, pH 10, (spectrum A; it includes about 10% of H-adduct absorption) and in N2O/O2 (1:1) saturated solution after pulse (spectrum B1) and 400 µm after pulse (spectrum B2). OD/cm values are normalized to 10 Gy.

**Fig. 4.** Transient absorption spectra obtained in N2O saturated aqueous solution of 5 × 10^{-4} mol dm^{-3} chlorobenzene, pH 9.3, (spectrum A; it includes about 10% of H-adduct absorption) and in N2O/O2 (1:1) saturated solution after pulse (spectrum B1) and 400 µm after pulse (spectrum B2). OD/cm values are normalized to 10 Gy.
3. Results and discussion

3.1. Pulse radiolysis

\textit{N}_{2}O saturated characteristics:} To define the spectroscopic and kinetic characteristics of the intermediates formed immediately after the reactions of \textsuperscript{•}OH radicals with 2-, 3-, 4-chlorobenzoic acids and chlorobenzene electron pulse radiolysis experiments in \textit{N}_{2}O saturated solutions were performed. By the radiolysis of water \textsuperscript{•}OH radicals, solvated electrons, \textit{e}_{aq}, and H-atoms, gross reaction (1), are produced:

\[ \text{H}_2\text{O} \rightarrow \text{•OH, H}_2, \text{H}_2\text{O}_2, \text{H}_3\text{O}^+ + \text{H}^- \] \hspace{1cm} (1)

The radiation chemical yields (G-values) of the primary radicals are \( G(\text{•OH}) \approx G(\text{\textit{e}_{aq}}) \approx 0.29 \text{ mmol J}^{-1} \) and \( G(\text{H}^+) \approx 0.06 \text{ mmol J}^{-1} \). In \textit{N}_{2}O saturated solutions \( \text{e}_{aq} \) are converted into \textsuperscript{•}OH radicals, reaction (2):

\[ \text{e}_{aq} + \text{N}_2\text{O} \rightarrow \text{•OH} + \text{H}^+ + \text{N}_2 \] \hspace{1cm} (2)

Thus in the pH range 4–10 the yield of hydroxyl radicals is \( G(\text{•OH}) \approx 0.58 \text{ mmol J}^{-1} \). The principal reaction of hydroxyl radicals with benzoic acids is addition to the ring to form carboxylated hydroxycyclohexadienyl radicals (OH-adducts). This is shown for one possible OH-adduct of 4-ClBzA (C3 position) in reaction (3):

![Diagram](image)

\[ \text{COO}^- + \text{•OH} \rightarrow \text{COO}^- + \text{Cyclohexadienyl radical} \] \hspace{1cm} (3)

The transient absorption spectra for the OH-adducts (including that of \( \sim 10\% \) H-adduct absorption) of 2-, 3-, 4-ClBzA and ClBz are presented in the Figs. 1–4, spectra A. All have broad absorption bands, a shoulder at 305–322 nm and maxima in the range of 320–340 nm, whereby the shift to longer wavelengths is in the sequence ClBz < 2-ClBzA < 3-ClBzA < 4-ClBzA. For calculation of the molar extinction coefficients the participation of H-adduct absorptions \((\text{Zona et al.}, 2008)\) were considered. The rate constants, \( k(\text{•OH}+\text{S}) \), were determined from the kinetic profiles of the hydroxycyclohexadienyl radicals at the corresponding wavelength maxima. All OH-adducts disappeared according to a pure second-order reaction, \( 2k \sim (1–9) \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \), mainly by dimersization and/or disproportionation. The most probable reaction products formed due to the disproportionation reactions of the OH-adducts on the C2- and C3-position of 4-ClBzA are 4-Cl2OHBzA and 4-Cl3OHBzA. This is shown for the OH-adduct on the C3-position of 4-ClBzA reaction (4):

![Diagram](image)

\[ \text{COO}^- + \text{•OH} \rightarrow \text{COO}^- + \text{H}_2O \] \hspace{1cm} (4)

The spectroscopic and kinetic data, together with the literature \( k(\text{•OH}+\text{S}) \) values, are summarized in Table 1. As is obvious, the rate constants of \textsuperscript{•}OH with 2-ClBzA and 3-ClBzA measured by competition method, \text{Shamdasani et al.}, 1974, are somewhat lower than those obtained in this work, that for 4-ClBzA and ClBz are in good agreement with the reported values. A calculation of the molar extinction coefficient at \( \lambda_{\text{max}} \) of the OH-adducts of chlorobenzene without correcting for H-adduct contribution yielded the same value, \( \epsilon_{\text{max}} \approx 4600 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1} \), as that reported from \textit{Merga et al.}, 1994.

\textit{N}_{2}O/O_{2} saturated solutions:} In the presence of oxygen the formation of H-adducts is prevented due to the fast reaction of H-atoms with oxygen, reaction (5a):

\[ \text{H}^+ + \text{O}_2 \rightarrow \text{HO}_2^- \quad k_{\text{5a}} = 2.1 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \quad (\text{Buxton et al., 1988}) \] \hspace{1cm} (5a)

\[ \text{HO}_2^- \rightarrow \text{H}^+ + \text{O}_2^- \quad \text{pK} = 4.8 \quad (\text{Getoff and Prucha, 1983}) \] \hspace{1cm} (5a)

\textbf{Table 1}

<table>
<thead>
<tr>
<th>Substrate</th>
<th>OH-adducts spectroscopic data</th>
<th>Rate constants (dm\textsuperscript{3}mol\textsuperscript{-1}s\textsuperscript{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \lambda_{\text{max}} ) (nm)</td>
<td>( \epsilon_{\text{max}} ) (dm\textsuperscript{3}mol\textsuperscript{-1}cm\textsuperscript{-1})</td>
</tr>
<tr>
<td>2-ClBzA</td>
<td>315</td>
<td>3800</td>
</tr>
<tr>
<td>3-ClBzA</td>
<td>325</td>
<td>4000</td>
</tr>
<tr>
<td>4-ClBzA</td>
<td>322</td>
<td>4400</td>
</tr>
<tr>
<td>ClBz</td>
<td>305</td>
<td>3600</td>
</tr>
</tbody>
</table>

\( ^a \) Shamdasani and Rao (1974).

\( ^b \) Elovitz and von Gunten (1999).

\( ^c \) Mezyk et al., 2008 (temperature: 21 °C)

\( ^d \) Ashton et al. (1995) (temperature 20 °C)
In solutions saturated with N₂O/O₂ (1:1 v/v) addition of oxygen to the OH-adducts under formation of hydroxycyclohexadienylperoxyl radicals is to be expected. One possible peroxyl-radical is given for the OH-adduct on position C3 of 4-ClBzA in reaction (6):

\[
\begin{align*}
\text{Cl} & \quad \text{H} \\
\text{COO}^- & \quad \text{OH} \\
\text{Cl} & \quad \text{H} \\
\text{OH} & \quad \text{Cl} \\
\text{H} & \quad \text{O}_2 \\
\text{H} & \quad \text{O}_2 \\
\text{Cl} & \quad \text{H} \\
\text{OH} & \quad \text{Cl} \\
\text{H} & \quad \text{O}_2 \\
\text{Cl} & \quad \text{H} \\
\text{OH} & \quad \text{Cl} \\
\end{align*}
\]

Peroxyl-radical formation was detectable for 2-, 4-ClBzA and ClBz. The pseudo-first order decay at the OH-adduct maxima (325, 340 and 320 nm) was in correlation with an absorption build up in the short wavelength range (280, 290 and 270 nm, respectively). The oscilloscope traces for 4-ClBzA are depicted in Fig. 5. The fast reaction with oxygen is also reflected in the strong decrease in the OH-adduct absorptions in N₂O/O₂ saturated solutions, for 2-ClBzA it is 33% and for 4-ClBzA 38% (Figs. 1 and 3, spectra B1). For the OH-adducts of 3-ClBzA this reduction is only 13% (Fig. 2, spectrum B1), whereby the major part of it can be attributed to the missing H-adducts reaction (5a). The reaction of the 3-ClBzA OH-adduct transients with oxygen was too slow to be recorded with the pulse radiolysis set up. All rate constants,

![Fig. 5. Kinetic profiles of the disappearance (A) of the OH-adduct absorption of 4-ClBzA by reaction with O₂ (340 nm) and the formation (B) of the corresponding peroxyl radical (290 nm). Solution: 2.5 \times 10^{-4} \text{ mol dm}^{-3} \text{ 4-ClBzA, pH 10, 0.6 \times 10^{-3} mol dm}^{-3} \text{ O}_2 \text{ and } 14 \times 10^{-4} \text{ mol dm}^{-3} \text{ N}_2\text{O. Dose: 5 Gy/0.4 \mu s pulse.}](image-url)
k(OH-adducts + O₂), are summarized in Table 1, the transient absorption spectra obtained under N₂O/O₂ conditions after pulse end and 400 μs after pulse are presented in the Figs. 1–4, spectra B1 and B2.

3.2. Gamma-radiolysis and product analysis

3.2.1. N₂O saturated solutions

To determine the yields of degradation, dechlorination and product formations initiated by OH radicals gamma-radiolysis was carried out. The decrease in 2-, 3- and 4-ClBzA and the chloride release as a function of dose are shown in Fig. 6. The rates for degradation are comparable for all ClBzAs with initial decreases of \( G_i = 0.50–0.52 \text{ mol J}^{-1} \) (Table 2), which is ~10% lower than the OH-radical concentration. It can be supposed that the decay reactions of the OH-adducts via disproportionation induced a partial regeneration of the substrates e.g. reaction (4).

The chloride release is significantly higher for 3-ClBzA, \( G_i = 0.23 \text{ mol J}^{-1} \), whereas for 2- and 4-ClBzA only 0.15 \text{ mol J}^{-1} were found (Table 2). At the 50% degradation dose (0.50–0.60 kGy) the chloride concentration is ~85% higher for 3-ClBzA than for 2- and 4-ClBzA (Fig. 6). This might be referred to an addition of \( \cdot \text{OH} \) on the ipso-chloro-position of the 3-ClBzA molecule. Since OH radicals have electrophilic properties and the carboxylate group has a meta-directing effect, the positions C₃ and C₅ on the aromatic ring of the chlorobenzoic acids are slightly activated for \( \cdot \text{OH} \) addition. Therefore it can be assumed that in case of 3-ClBzA the share of an OH-adduct on C₃ position gained importance. Such transients are known to eliminate HCl.

![Fig. 6. Gamma-radiolysis of N₂O saturated solutions of chlorobenzoic acids (500 μmol, pH 9.2). Degradation of 2-, 3- and 4-ClBzA and formation of chloride (μmol) as a function of dose.](image)

### Table 2

<table>
<thead>
<tr>
<th>Substrate</th>
<th>N₂O  ( G_i(\cdot \text{OH}) = 0.58 \text{ mol J}^{-1} )</th>
<th>Air  ( G_i(\cdot \text{OH}) = 0.29 \text{ mol J}^{-1} )</th>
<th>O₂   ( G_i(\cdot \text{OH}) = 0.29 \text{ mol J}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( G_i = \text{μmol J}^{-1} )</td>
<td>( G_i = \text{μmol J}^{-1} )</td>
<td>( G_i = \text{μmol J}^{-1} )</td>
</tr>
<tr>
<td>4-ClBzA</td>
<td>-0.52 ± 0.04</td>
<td>-0.37 ± 0.03</td>
<td>-0.28 ± 0.02</td>
</tr>
<tr>
<td>4-C130HBzA</td>
<td>0.042 ± 0.005</td>
<td>0.042 ± 0.005</td>
<td>0.036 ± 0.005</td>
</tr>
<tr>
<td>4-C120HBzA</td>
<td>0.22</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4-C1POHb</td>
<td>0.021 ± 0.003</td>
<td>-0.01</td>
<td>0.007 ± 0.002</td>
</tr>
<tr>
<td>4-OHBzA</td>
<td>-</td>
<td>0.042 ± 0.005</td>
<td>0.016 ± 0.005</td>
</tr>
<tr>
<td>Chloride</td>
<td>0.15 ± 0.02</td>
<td>0.31 ± 0.03</td>
<td>0.22 ± 0.02</td>
</tr>
<tr>
<td>3-ClBzA</td>
<td>-0.50 ± 0.05</td>
<td>-0.22 ± 0.015</td>
<td>-0.17 ± 0.015</td>
</tr>
<tr>
<td>3-C140HBzA</td>
<td>0.01</td>
<td>0.026 ± 0.003</td>
<td>0.047 ± 0.004</td>
</tr>
<tr>
<td>3-C60HBzA</td>
<td>0.035 ± 0.003</td>
<td>0.042 ± 0.003</td>
<td>0.057 ± 0.005</td>
</tr>
<tr>
<td>Chloride</td>
<td>0.23 ± 0.02</td>
<td>0.15 ± 0.02</td>
<td>0.083 ± 0.01</td>
</tr>
<tr>
<td>2-ClBzA</td>
<td>-0.52 ± 0.05</td>
<td>-0.30 ± 0.03</td>
<td>-0.27 ± 0.02</td>
</tr>
<tr>
<td>Chloride</td>
<td>0.15 ± 0.02</td>
<td>0.23 ± 0.02</td>
<td>0.17 ± 0.02</td>
</tr>
</tbody>
</table>

Solutions: 5 × 10⁻⁴ mol dm⁻³ 2-, 3- and 4-chlorobenzoic acid, pH 9.2; N₂O saturation: [N₂O]=2.8 × 10⁻² mol dm⁻³, presence of air: [O₂]=0.25 × 10⁻³ mol dm⁻³, oxygen saturation: [O₂]=1.25 × 10⁻¹ mol dm⁻³.

* Presence of K₃Fe(CN)₆
via first order- reaction (7a) and second order (e.g. reaction (7b)) reactions (Latif et al., 1978; Merga et al., 1994; Quint et al., 1996).

\[
\text{H}^+ + \text{Cl}^- + \text{OH} \rightarrow \text{HCl} + \text{O} \cdot + \text{H} \cdot \ 
\text{(7a)}
\]

\[
\text{H}^+ + \text{Cl}^- + \text{OH} \rightarrow \text{2HCl} + \text{5Cl}^- + \text{5O} \cdot \ 
\text{(7b)}
\]

The quantitative determination of products by HPLC is only achievable by comparison with reference compounds. The most probable chlorinated hydroxybenzoic acids arising from 2-ClBzA are 2-Cl3OHBzA and 2-Cl5OHBzA. Since they were not available their identification/quantification was not possible. In case of 3-ClBzA the compounds 3-Cl4OHBzA and 3-Cl6OHBzA (i.e. 5-chlorosalicylic acid) were at disposal, their formation occurred with \( G_i = \text{0.01 mol J}^{-1}/\text{C0} \). For 4-ClBzA the hydroxylation products 4-Cl3OHBzA and 4-Cl2OHBzA reaction (4) as well as 4-ClPhOH were detectable (Table 2). Compared to the decomposed quantities of the substrates, the yields of the hydroxylation products were very low. At the 50% degradation dose 11 \( \mu \text{mol} \) 3-Cl4OHBzA and 5 \( \mu \text{mol} \) 3-Cl6OHBzA could be found for 3-ClBzA, and 20 \( \mu \text{mol} \) 4-Cl3OHBzA, 5 \( \mu \text{mol} \) 4-Cl2OHBzA and 7 \( \mu \text{mol} \) 4-ClPhOH for 4-ClBzA. The latter might be formed by an \(^{\prime}\)OH induced decarboxylation occurring at least partially via postirradiation effects, as was reported for benzoic acid by Klein et al., 1975. These results prove that the primarily formed \(^{\prime}\)OH-adduct-radicals are disappearing very fast in second order reactions, before hydroxylation products can be formed. To get a better insight into the initial pattern of the \(^{\prime}\)OH addition on 4-ClBzA, \( K_{3\text{Fe(CN)}_6} \) was used to oxidize the non-ipso-\(^{\prime}\)OH-adducts to the corresponding phenols (Buxton et al., 1986). Besides the meta directing effect of \(-\text{COO}^-\) the chlorine substituent, although electron withdrawing, has an ortho-para directing effect, making the C3/C5 positions of 4-ClBzA to a favourite reaction site for an \(^{\prime}\)OH attack. This could be confirmed by the yields of 4-ClBzA in the presence of the oxidant, which increased more than five fold to \( G_i = \text{0.22 mol J}^{-1}/\text{C0} \). This value is in good agreement with the yield of 3-hydroxybenzoic acid found after radiolysis of benzoic acid in the presence of ferricyanide (Klein et al., 1975). The initial yields (\( G_i \)-values), obtained from the linear part of the yield vs. dose plots, for substrate degradation, products and chloride formation in \( N_2O \) saturated solutions are summarized in Table 2.

### 3.2.2. Presence of oxygen

In the presence of oxygen (aerated: \([O_2]\) = 0.25 \( \times 10^{-3} \) mol dm\(^{-3}\), oxygen saturated: \([O_2]\) = 1.25 \( \times 10^{-3} \) mol dm\(^{-3}\)) H-atoms reaction (5a,b) and electrons reaction (8) are scavenged, delivering superoxide radicals, \( G(O_2^-) \approx 0.34 \mu \text{mol} J^{-1}/\text{C0} \).

\[
\text{e}_{aq} + \text{O}_2^- \rightarrow \text{O}_2 \cdot + \text{e}_{aq} \ 
\text{(8)}
\]

Generally superoxide radicals are reacting slowly with aromatic compounds (e.g. \( k(O_2^- + \text{tyrosin}) < 10 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}\), Bielski et al., 1985), leaving the \(^{\prime}\)OH radicals as the principle reactive species. To evaluate the influence of oxygen concentration on the \(^{\prime}\)OH-radical induced processes, experiments under aerated and oxygenated conditions were performed. The aerated solutions were investigated, because commonly these are the conditions when ionizing radiation is applied as method for degradation of water pollutants.

#### 3.2.2.1. Degradation and dechlorination. Aerated solutions

The decomposition and the chloride release in the presence of air for 2-, 3- and 4-ClBzA as a function of dose are shown in Fig. 7. The initial yields of degradation and product formation are summarized in Table 2. In contrast to \( N_2O \) saturated solutions, where the degradation rates were similar for all ClBzAs, in the presence of air the decay and the chloride release for 4-ClBzA was by far the
The initial decrease, $G_i = 0.37 \mu$mol J$^{-1}$, was much higher than $G(\cdot \text{OH})$. This could be referred to a participation of $\text{e}^-_{\text{aq}}$ to the degradation and dehalogenation process. Taking into account the concentration of O$_2$ in air, the rate constants of $\text{e}^-_{\text{aq}}$ with oxygen reaction (8) and with 4-ClBzA, $k(e^-_{\text{aq}} + 4\text{-ClBzA}) = 6 \times 10^9$ dm$^3$ mol$^{-1}$ s$^{-1}$ (Zona et al., 2008), one can calculate that $\sim 40\%$ of the $\text{e}^-_{\text{aq}}$ are consumed in reactions with 4-ClBzA. The $\text{e}^-_{\text{aq}}$ react quantitatively with 4-ClBzA whereby chloride and carboxyphenyl radicals are formed, reaction (9a,b). The intermediate radical anions $\text{ClBzA}^{\cdot -}$ reaction (9a) were only observable for 3-ClBzA (Zona et al., 2008).

$\text{ClC}_6\text{H}_4\text{COO}^- + \text{e}^-_{\text{aq}} \rightarrow [\text{ClC}_6\text{H}_4\text{COO}^{\cdot -}]$  
$\rightarrow \text{Cl}^- + \cdot \text{C}_6\text{H}_4\text{COO}^-$ (9a,b)

In case of 2-ClBzA the initial decrease was only slightly higher than OH-radical concentration because this compound reacts much slower with $\text{e}^-_{\text{aq}}$, $k(e^-_{\text{aq}} + 2\text{-ClBzA}) = 1.4 \times 10^9$ dm$^3$ mol$^{-1}$ s$^{-1}$ (Zona et al., 2008), therefore their participation was expected to be $< 15\%$. For 3-ClBzA the initial yield of degradation was below

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**Fig. 8.** Gamma-radiolysis of oxygen saturated solutions of chlorobenzoic acids (500 µmol, pH 9.2). Degradation of 2-, 3- and 4-ClBzA and formation of chloride (µmol) as a function of dose.

**Fig. 9.** Gamma-radiolysis of aerated and oxygenated solutions of 3-ClBzA (500 µmol, pH 9.2). Formation of phenolic products (µmol) as a function of dose.
However, a contribution of \( \sim 35\% \) \( e_{aq} \) to the decomposition process has to be assumed due to the fast reaction \( k(e_{aq}^+ + 3\cdot \text{ClBzA}) = 4.8 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \) (Zona et al., 2008). The sequence of degradation and dechlorination was 4-ClBzA \( \rightarrow \) 2-ClBzA \( \rightarrow \) 3-ClBzA. 

**Oxygenated solutions:** Accordant with the five fold higher oxygen concentration an involvement of the \( e_{aq} \) in reactions with the substrates was of minor importance ( \( \sim 5\% \) for 2-ClBzA and \( \sim 10\% \) for 3- and 4-ClBzA). This is reflected in the lower yields for decomposition and chloride release (Table 2). The rates of degradation were practically the same for 2- and 4-ClBzA, and their initial decrease equaled the \( ^\circ \text{OH} \) concentration, Fig. 8 and Table 2. Their dehalogenation rates were very similar at low doses, yet with increasing dose that of 2-ClBzA retarded markedly. The initial yield of the 3-ClBzA decrease, \( G(\text{Cl}) = 0.22 \), is considerably lower than \( G(\text{Cl}) \) implying that although oxygen is present regeneration reactions of the substrate take place. A comparison of the initial yields of the chloride release of 3-ClBzA in oxygenated and in \( \text{N}_2\text{O} \) saturated solution revealed that in the former it is 49% referred to the decomposed acid, and in the latter it is with 46% very similar, indicating that the presence of oxygen does not markedly affect the dechlorination. This is in accordance with the pulse radiolysis results, where no reaction of \( \text{O}_2 \) with the \( \text{OH} \)-adducts of 3-ClBzA was observible (Table 1). Therefore it might be concluded that the decay reactions of the ipso-adducts, reactions (7a) and (7b), in particular the first order decay, reaction
(7a), occur faster than their reaction with O₂. The order of degradation and dehalogenation in oxygenated solution was 4-ClBzA > 2-ClBzA > 3-ClBzA.

3.2.2.2. Product formation. Aerated and oxygenated solutions: For 3-ClBzA the dose dependence of the yields of the hydroxylation products 3-Cl6OHBzA and 3-Cl4OHBzA and their initial G-values are given in Fig. 9 and Table 2. These compounds are formed due to the fast reaction of oxygen with the carbon centred radicals of the OH-adducts followed by a HO₂⁻ splitting, as shown for 3-Cl6OHBzA in reaction (10).

\[
\text{HO}_2^->\text{HO}_2^->\text{ClBzA} \rightarrow \text{Cl6OHBzA} \quad (10)
\]

The overall yields of both compounds were lower in aerated solutions because of the participation of e⁻/CO₂ in the radiolysis process. Whereas in aerated solutions at a dose of 0.7 kGy the formation curve of 3-Cl6OHBzA flattened and the production of 3-Cl6OHBzA decreased, in oxygenated solution both products were formed also at higher doses via reaction (10) as a result of the sufficient oxygen concentration (Fig. 9).

The formation of irradiation products from 4-ClBzA is depicted in Fig. 10. In oxygenated solutions the product distribution reflected to some extent the initial distribution of OH-adducts, i.e. higher yields from OH-adducts on positions C2/C3 and low yields from those formed on the ipso-positions at C1 and C4. Their concentrations were 4-Cl3OHBzA ≫ 4-Cl2OHBzA ≫ 4-OHBzA ≫ 4-ClPhOH. In aerated solution the participation of e⁻/CO₂ on product formation was markedly discernible. The relatively high amounts of 4-OHBzA might result from carboxyphenyl radicals formed by reaction (9a,b), followed by a reaction with oxygen. As soon as the oxygen was consumed (at about 0.6 kGy), the production of 4-OHBzA decreased and the formation of benzoic acid increased. The latter is the main organic product formed by radiolysis of 4-ClBzA in oxygen free solution (Zona et al., 2008).

3.2.3. Total degradation and toxicity (aerated solutions)

The degradation rates for 500 μmol of the ClBzAs were very different. At 1 kGy the following decomposed quantities were detected: 315 μmol (4-ClBzA), 265 μmol (2-ClBzA) and 221 μmol (3-ClBzA), Fig. 7. Referred to these decomposed amounts the percentage formations of chloride, however, were comparable: 61%, 65% and 62%, respectively. With a dose of 5 kGy total removal of all chlorobenzoic acids was achieved i.e. their concentrations were beyond the detection limit of the HPLC system, < 1 μmol. At 5 kGy the chloride concentrations were 400–425 μmol, it means that still ~20% chloroorganic compounds are present, which may be hazardous for the environment.

Since during irradiation of the ClBzAs several phenolic compounds were formed (some of them could be detected, Figs. 9, 10; Table 2), the alteration of the acute toxicity depending on dose was determined. The toxicity measurement is based on the inhibition of the bioluminescence of Vibrio bacteria strains after 30 min of incubation, %I₃₀, by toxic water components. An inhibition of ≤ 20% can be regarded as non toxic. Chlorobenzoic acids are moderately toxic (4-ClBzA: EC₅₀=68 mg/dm³, 3-ClBzA: EC₅₀=109 mg/dm³; EC₅₀ is the effective concentration that is needed to reduce bacterial luminescence by 50%), compared to chlorophenols (4-ClPhOH: EC₅₀=1.2 mg/dm³, Zona et al., 1999). The initial inhibition for the starting solution of 500 μmol 4-ClBzA was 40%, upon irradiation it increased and reached a maximum at ~1 kGy with 72% inhibition, indicating the formation of toxic radiolytic products. The concentrations of the detectable phenolic compounds at this dose were: 19 μmol 4-Cl3OHBzA, 10 μmol 4-Cl2OHBzA, 16 μmol 4-OHBzA and 11 μmol 4-ClPhOH (Fig. 10, air). Then it decreased continuously and only at 4.9 kGy it dropped beyond the critical value of 20% (Fig. 11). The course of the inhibition (%I₃₀) vs. dose curve was very similar for 3-ClBzA, the 2-ClBzA solutions did not show an inhibition effect.

![Fig. 11. Toxicy, given as inhibition of bioluminescence in percentage (%I₃₀), of 500 μmol 4-ClBzA as a function of dose.](image-url)
4. Conclusion

In a previous paper (Zona et al., 2008) we investigated the reactions of H atoms and hydrated electrons with monochlorobenzoic acids. The present work was directed to the oxidation of these compounds. A comprehensive insight into the reaction mechanisms of the oxidation processes initiated by OH radicals under various radiation conditions (N2O, air, oxygen) was obtained. Pulse radiolysis results were contrasted with that of steady-state radiolysis.

The individual monochlorobenzoic acids showed clearly different degradation efficiencies in the presence of oxygen. A comparison of the results for dechlorination at 1 kGy revealed that, referred to the decomposed quantities of the ClBzAs, the chloride formation for 2- and 4-ClBzA in oxygen free medium (N2O) was only 29% and 33%, whereas in aerated solutions it approximately doubled to 65% and 61%, respectively. In case of 3-ClBzA the increase was only 7%, from 55% (N2O) to 62% (air). The reason for the enhanced decomposition of 2- and 4-ClBzA could be elucidated by pulse radiolysis. The OH-adducts of these compounds reacted very fast by addition of O2. Thereby peroxy radicals were formed inducing an intensified oxidative degradation process. In case of the 3-ClBzA-OH-adducts no reaction with O2 was measurable by pulse radiolysis.

Concerning the use of gamma-radiolysis as method for the removal of halogenated aromatic substances in water it can be summarized that in aerated solution total degradation of the monochlorobenzoic acids could be achieved. However, due to the formation of toxic compounds during irradiation toxicity measurements should be carried out to evaluate the quality of the irradiated samples.

References


