•OH Radical-induced oxidation of chlorobenzene in aqueous solution in the absence and presence of oxygen

Getahun Merga,[a] H.-P. Schuchmann,[a] B. S. Madhava Rao[b] and Clemens von Sonntag *,[a]

[a] *Max-Planck-Institut für Strahlenchemie, Stiftstr. 34-36, PO Box 131065, D-45470 Mülheim an der Ruhr, Germany*

[b] *Department of Chemistry, University of Pune, Pune 411007, India*

The reaction of hydroxyl radicals, generated radiolytically in N_2O-containing aqueous solutions [$G(^{\bullet}OH) \approx 5.8 \times 10^{-7}$ mol J^{-1}], with chlorobenzene has been studied. In the presence of $Fe(CN)_6^{3-}$ the major products (G values in units of 10^{-7} mol J^{-1} in parentheses) are 2-chlorophenol (2.5), 3-chlorophenol (1.25) and 4-chlorophenol (1.75). Pulse radiolysis with conductometric detection (in the absence of the oxidant) shows that prompt HCl formation (which occurs upon •OH radical addition at the *ipso*-position) is only a very minor process (0.03), and it is concluded that •OH radical addition to the *ortho*:*meta*:*para*:*ipso* positions occurs in a proportion of 1:0.5:0.7: < 0.01, *i.e.* there is a noticeable preference of attack at the *para* and *ortho* positions and a considerable steric hindrance of the addition to the *ipso* position. In the absence of the oxidant, the yield of the chlorophenols is low [G(total chlorophenols) = 0.4×10^{-7} mol J^{-1}] and dimeric products [bis(hydroxychlorocyclohexadienyls)] predominate. Most of these primary dimers are unstable and rearomatize under dehydration, which can be promoted by heating at pH 1, to various dichlorobiphenyl, chlorohydroxybiphenyl and dihydroxybiphenyl isomers.

In the presence of O_2, the chlorohydroxycyclohexadienyl radicals are (reversibly) converted into the corresponding peroxyl radicals ($k_{forward} = 2.6 \times 10^8$ dm^3 mol^{-1} s^{-1}; $k_{reverse} = 5.5 \times 10^4$ s^{-1}). Out of this equilibrium two reactions occur ($k_{product\ formation} = 1.1 \times 10^3$ s^{-1}): HO_2-elimination leading to the three isomers of chlorophenol [G(chlorophenol total) = 2.1×10^{-7} mol J^{-1}] and formation of *endo*-peroxidic structures which in turn are converted into peroxyl radicals and subsequently undergo fragmentation. Most of these products, which number in excess of 30 by GC analysis, are free of chlorine [G(chloride ion) = 3.3×10^{-7} mol J^{-1}], apart from a few which contain the vinyl chloride function.

There is mounting interest in the reactions of •OH radicals in aqueous solutions. For drinking water and waste water remediation, the so-called *Advanced Oxidation Processes* (O_3–H_2O_2, H_2O_2–UV, O_3–UV, electron beam) make use of the high reactivity of this intermediate (for rate constants, see ref. 1).[2–5] This is of special interest in the case of pollutants which react only slowly with ozone (for rate constants see ref. 6) which is the most common oxidant in water processing. Aromatic compounds, except for those with electron-donating substituents, belong to the class of ozone-refractory species. The goal in using these *Advanced Oxidation Processes* is to mineralize the pollutants as far as possible, and in the case of chlorine-containing pollutants it is of special importance that no chlorine-containing products be formed that might be toxic or impart an adverse taste and odour. Model studies are a prerequisite for a better understanding of the elementary steps in the oxidation processes and for assessing the requirements in water remediation plants (*e.g.* the amount of oxidant required for effective mineralization). In the present study we have chosen chlorobenzene as the model pollutant as it combines the aromatic character with the halogen content. Some of its •OH-radical-induced chemistry can be based on what is known from benzene[7,8] and other aromatic compounds.[9,10]

Experimental

Chlorobenzene (Fluka) was used as received. Solutions were made up in Millipore Milli-Q filtered water presaturated with N_2O or N_2O–O_2 (4:1 v/v) (Messer Griesheim) prior to the addition of chlorobenzene.

γ-Radiolysis was carried out with a ^{60}Co γ-source at a dose rate of 0.17 Gy s^{-1} as determined by Fricke dosimetry. The pulse radiolysis set-up (2.8 MeV Van de Graaff electron generator; 0.4–2 μs pulse width) has been described before.[11]

The products formate, glycolate, glyoxylate and chloride were determined by ion chromatography [Dionex 2010i; IonPac AS9-SC 4 mm with precolumn HPIC-AG4; eluent: (2.0–0.5) × 10^{-3} mol dm^{-3} $NaHCO_3$ at 10^{-3} mol dm^{-3} min^{-1}]. The yields of the products *o*-, *m*- and *p*-chlorophenol were determined by HPLC (Merck-Hitachi 655A-22, L-6200A; column: Nucleosil C-18, 25 cm; eluent: 40% methyl alcohol, 14% acetonitrile containing 0.04 mol dm^{-3} phosphate buffer pH ≈ 4.0, at 10^{-3} dm^3 min^{-1}). Reference material was commercially available (Fluka).

The products formed under anoxic conditions were extracted into diethyl ether with a Ludwig extractor (Normag), dried (sodium sulfate), concentrated, trimethylsilylated with *N*,*N*-bis(trimethylsilyl)trifluoroacetamide (BSTFA; Macherey Nagel) and analysed by gas chromatography–mass spectrometry [GC–MS; Hewlett-Packard HP 5890 Series II gas chromatograph, 5971A mass selective detector; column: 12 m × 0.2 mm HP-Ultra 1 (crosslinked silicone gum), temperature programmed, 60–270 °C]. Although the MS fragmentation pattern (electron impact 70 eV) is practically the same for the various isomers of a particular product compound, the relative peak intensities may differ noticeably between the isomers. Typical mass spectra are compiled in Table 1. 4,4′-Dihydroxybiphenyl was available as a reference material. For quantitation the yields of the products were related to that of *p*-chlorophenol (flame ionization detection).

The products formed in the presence of O_2 are hydrophilic. Typically, they contain hydroxyl and carbonyl groups (*cf.* ref. 8). The latter can be reduced by $NaBH_4$ or $NaBD_4$. Upon $NaBD_4$ reduction, a deuterium atom is incorporated into the

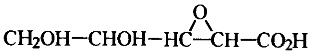
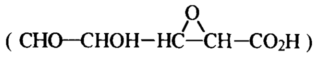
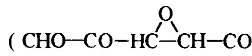
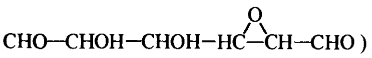
Table 1 Mass spectra and their assignment to the products formed in the γ-radiolysis of N_2O-saturated aqueous solutions of chlorobenzene. The OH groups are trimethylsilylated. The chlorine containing *m*/*z* signals are marked by an asterisk (two asterisks in case of two chlorine atoms). The letters **a**–**h** refer to the chromatograms shown in Figs. 1 and 2

Compound	*m*/*z* (%)
Chlorobiphenyl MW 188	188* (100), 152 (47), 76 (26)
2-Chlorophenol (TMS) **a** MW 200	200* (26), 185* (90), 149 (73), 93* (100), 73 (18)
3-Chlorophenol (TMS) **b** MW 200	200* (31), 185* (100), 149 (4), 93* (18), 73 (23)
4-Chlorophenol (TMS) **c** MW 200	200* (37), 185* (100), 149 (4), 93* (11), 73 (18)
x,*x*′-Dichlorobiphenyls **d** MW 222	222** (100), 186* (7), 152 (54), 75 (13)
x-Chloro-*x*′-hydroxybiphenyls (TMS) **e** MW 276	276* (38), 261* (30), 245* (11), 211 (11), 168 (11), 152 (13), 139 (8), 93* (100), 73 (22)
x-Chloro-*y*-hydroxycyclohexadienylchlorobenzenes (TMS) **f** MW 312	312** (23), 277* (58), 222** (4), 152 (23), 93* (12), 73 (100)
x,*x*′-Dihydroxybiphenyls (*bis*TMS) **h** MW 330	330 (100), 315 (14), 150 (20), 73 (63)
x-Chloro-*y*-hydroxycyclohexadienylphenols (*bis*TMS) **g** MW 366	366* (10), 331 (28), 276 (15), 261* (13), 152 (4), 147 (10), 93* (23), 73 (100)

Table 2 Mass spectra of TMS-derivatives and assignments to the products formed in the γ-radiolysis of N_2O–O_2-saturated aqueous solutions of chlorobenzene[a]

RT/min	TMS ethers of polyhydric alcohols (and their precursors)	*m*/*z* (%)
5.2	$\mathrm{CH_2OH{-}CHOH{-}CH_2OH}$ MW 308 ($\mathrm{CHO{-}CO{-}CHO}$, $\mathrm{CHO{-}CO{-}CH_2OH}$, $\mathrm{CHO{-}CHOH{-}CH_2OH}$)	$NaBH_4$: 293(2), 218 (16), 205 (45), 147 (68), 133 (37), 117 (42), 103 (21), 73 (100); $NaBD_4$: 295 (1), 296 (2), 220 (11), 221 (10), 205 (10), 206 (20), 207 (30), 147 (70), 133 (30), 118 (12), 119 (23), 103 (10), 104 (12), 73 (100)
5.3	$\mathrm{CH_2OH{-}CH{=}CH{-}CO_2H}$ MW 246 ($\mathrm{CHO{-}CH{=}CH{-}CO_2H}$)	$NaBH_4$: 246 (3), 231 (11), 191 (3), 156 (20), 147 (100), 75 (25), 73 (55); $NaBD_4$: 247 (1), 232 (11), 157 (15), 147 (100), 75 (22), 73 (46)
5.4	$\mathrm{CH_2OH{-}CH{=}CH{-}CH{=}CH{-}CH_2OH}$ MW 258 ($\mathrm{CHO{-}CH{=}CH{-}CH{=}CH{-}CH_2OH}$, $\mathrm{CHO{-}CH{=}CH{-}CH{=}CH{-}CHO}$)	$NaBH_4$: 258 (22), 257 (15), 243 (10), 169 (30), 147 (66), 73 (100); $NaBD_4$: 260 (5), 259 (12), 258 (12), 244 (2), 243 (2), 215 (13), 171 (6), 170 (25), 169 (15), 147 (66), 73 (100)
5.6	$\mathrm{CH_2OH{-}CH{=}CCl{-}CH_2OH}$ MW 266 ($\mathrm{CHO{-}CH{=}CCl{-}CHO}$)	$NaBH_4$: 231 (7) 191 (40), 176* (37), 147 (55), 103 (17), 93* (41), 73 (100); $NaBD_4$: 268* (1), 253 (1), 233 (4), 192 (16), 191 (10), 178* (43), 177* (33), 147 (100), 104 (11), 103 (4), 93* (36), 73 (100)
6.1	$\mathrm{CH_2OH{-}CHOH{-}CO_2H}$ MW 322 ($\mathrm{CHO{-}CO{-}CO_2H}$, $\mathrm{CHO{-}CHOH{-}CO_2H}$)	$NaBH_4$: 307 (9), 292 (39), 205 (12), 189 (53), 147 (64), 133 (42), 117 (14), 103 (14), 73 (100); $NaBD_4$: 309 (4), 308 (4), 293 (25), 292 (12), 207 (6), 206 (5), 147 (67), 133 (33), 117 (8), 118 (8), 103 (12), 104 (13), 73 (100)
6.8	$\mathrm{CH_2OH{-}CH_2{-}CHOH{-}CH_2OH}$ MW 322 ($\mathrm{CHO{-}CH_2{-}CO{-}CHO}$)	$NaBH_4$: 232 (7), 219 (38), 189 (25), 147 (33), 133 (33), 103 (95), 73 (100); $NaBD_4$: 235 (1), 234 (2), 221 (50), 220 (20), 191 (12), 190 (15), 147 (50), 133 (26), 104 (70), 73 (100)
7.7, 7.8	(Chloro-5,6-dihydroxycyclohexa-1,3-diene) MW 290	$NaBH_4$ = $NABD_4$: 290* (13), 255 (16), 191 (18), 185* (5), 167 (9), 147 (29), 93* (18), 73 (100)
8.4, 8.9	$\mathrm{CH_2OH{-}CHOH{-}CH{=}CH{-}CH_2OH}$ MW 334 ($\mathrm{CH_2OH{-}CO{-}CH{=}CH{-}CHO}$)	$NaBH_4$: 244 (3), 231 (50), 155 (9), 147 (50), 142 (14), 133 (14), 103 (9), 73 (100) 69 (87); $NaBD_4$: 246 (2), 233 (36), 232 (12), 157 (8), 147 (52), 144 (14), 133 (16), 103 (8), 73 (100), 71 (48), 70 (15)
8.7, 9.0	(Chloro-3,6-dihydroxycyclohexa-1,4-diene) MW 290	$NaBH_4$: 255 (100), 185* (10), 167 (10), 147 (55), 93* (25), 73 (70); $NaBD_4$: GC-peaks too weak for running the mass spectra
8.8	$\mathrm{CH_2OH{-}CH_2{-}CH_2{-}CHOH{-}CH_2OH}$ MW 336 ($\mathrm{CHO{-}CH_2{-}CH_2{-}CO{-}CH_2OH}$, $\mathrm{CO_2H{-}CH_2{-}CH_2{-}CO{-}CH_2OH}$)	$NaBH_4$: 233 (8), 147 (27), 143 (100), 133 (18), 129 (9), 103 (6), 85 (15), 75 (20), 73 (82), 69 (19); $NaBD_4$: 236 (8), 235 (4), 147 (50), 146 (75), 145 (38), 133 (22), 131 (11), 105 (2), 104 (3), 103 (4), 88 (10), 73 (100)
9.5	Dihydroxychlorobenzene MW 288	$NABH_4$ = $NaBD_4$: 288* (64), 273* (26), 257* (54), 237 (42), 147 (15), 93* (18), 73 (100)
9.9, 10.1	$\mathrm{CH_2OH{-}CHOH{-}CHOH{-}CH_2OH}$ MW 410 ($\mathrm{CHO{-}CHOH{-}CHOH{-}CHO}$, $\mathrm{CH_2OH{-}CO{-}CO{-}CH_2OH}$, $\mathrm{CHO{-}CHOH{-}CO{-}CH_2OH}$)	$NaBH_4$: 320 (5), 307 (9), 217 (72), 205 (39), 189 (20) 147 (55), 117 (23) 103 (34), 73 (100); $NaBD_4$: 322 (2), 308 (10), 218 (44), 206 (28), 190 (10), 147 (60), 118 (21), 104 (15), 103 (10), 73 (100)
10.2	$\mathrm{CH_2OH{-}CH_2{-}CH{=}CH{-}CHOH{-}CH_2OH}$ MW 348 ($\mathrm{CHO{-}CH_2{-}CH{=}CH{-}CO{-}CH_2OH}$)	$NaBH_4$: 273 (7), 258 (4), 245 (4) 205 (33), 169 (3), 156 (11), 147 (62), 133 (14), 117 (50), 103 (10), 73 (100); $NaBD_4$: 275 (9), 260 (4), 247 (5), 206 (45), 157 (18), 147 (66), 133 (19), 118 (54), 104 (5), 103 (10), 73 (100)
10.3, 10.4	$\mathrm{CH_2OH{-}CH{=}CCl{-}CHOH{-}CH_2OH}$ MW 368 ($\mathrm{CHO{-}CH{=}CCl{-}CO{-}CHO}$) ($\mathrm{CHO{-}CH{=}CCl{-}CO{-}CH_2OH}$, $\mathrm{CHO{-}CCl{=}CH{-}CO{-}CH_2OH}$)	$NaBH_4$: 333 (1), 278(*) (2), 265* (18), 243 (4), 205 (4), 176* (11), 147 (36), 129 (100), 103 (11) 93* (15), 73 (90); $NaBD_4$ (at RT = 10.3): 335(1), 280* (1), 279* (1), 267* (13), 266* (10), 245 (1), 244 (1), 206 (2), 178* (7), 177* (7), 147 (41), 131 (75), 130 (50), 93* (12), 73 (100); (at RT = 10.4) 336 (1), 281* (< 1), 267* (15), 246 (1), 245 (1), 206 (2), 178* (12), 147 (35), 131 (100), 93* (18), 73 (92)
10.5	$\mathrm{CH_2OH{-}CHOH{-}CH{=}CH{-}CO_2H}$ MW 348 ($\mathrm{CH_2OH{-}CO{-}CH{=}CH{-}CO_2H}$)	$NaBH_4$: 333 (4), 318 (19), 292 (7), 245 (8), 205 (4), 156 (36), 147 (36), 133 (16), 103 (7) 73 (100); $NaBD_4$: 334 (2), 319 (18), 292 (3), 293 (3), 246 (8), 206 (3), 157 (34), 147 (44), 133 (18), 130 (18), 103 (9), 73 (100)

Table 2 (*continued*)

RT/min	TMS ethers of polyhydric alcohols (and their precursors)	m/z (%)
10.8	 $CH_2OH{-}CHOH{-}\overset{O}{HC{-}CH}{-}CO_2H$ MW 364  $(CHO{-}CHOH{-}\overset{O}{HC{-}CH}{-}CO_2H)$  $(CHO{-}CO{-}\overset{O}{HC{-}CH}{-}CO_2H)$	$NaBH_4$: 346 (3), 331 (7), 293 (8), 292 (18), 220 (8), 217 (8), 205 (11), 147 (48), 133 (9), 117 (9), 103 (7), 73 (100), $NaBD_4$: 294 (8), 293 (15), 292 (44), 221 (14), 220 (13), 218 (10), 207 (7), 206 (8), 147 (50), 133 (4), 118 (10), 104 (8), 73 (100)
11.3	$CH_2OH–CHOH–CH_2–CHOH–CH_2OH$ MW 424 $(CH_2OH–CO–CH_2–CHOH–CHO)$	$NaBH_4$: 321 (8), 231 (12), 205 (4), 189 (7), 147 (40), 129 (84), 117 (7), 103 (13), 73 (100), $NaBD_4$: 323 (8), 233 (11), 231 (5), 206 (4), 205 (5), 147 (50), 130 (91), 118 (5), 104 (12), 73 (100)
11.6	$CH_2OH–CHOH–CHOH–CH_2–CH_2OH$ MW 424 $(CHO–CHOH–CO–CH_2–CHO)$	$NaBH_4$: 307 (6), 219 (22), 205 (7), 191 (13), 147 (38), 129 (13), 117 (8), 103 (50), 73 (100), $NaBD_4$: 309 (2), 308 (4), 221 (16), 206 (5), 147 (35), 133 (18), 118 (11), 104 (32), 73 (100)
11.8	$CH_2OH–CH{=}CH–CH_2–CHOH–CO_2H$ or isomer MW 362 $(CHO–CH{=}CH–CH_2–CHOH–CO_2H$, or isomer)	$NaBH_4$: 347 (2), 331 (2), 272 (14), 259 (21), 215 (9), 204 (1), 147 (34), 133 (9), 127 (9), 103 (4), 73 (100), $NaBD_4$: 348 (2), 333 (1), 332 (1), 273 (16), 260 (28), 216 (10), 205 (1), 147 (44), 133 (12), 128 (9), 103 (7), 73 (100)
12.0	$CH_2OH–CH_2–CH{=}CCl–CHOH–CH_2OH$ MW 382 $(CO_2H–CH_2–CH{=}CCl–CO–CHO$	$NaBH_4$: 346 (1), 279* (29), 205 (4), 189 (20), 167* (8), 147 (32), 117 (7) 103 (51), 93* (10) 73 (100), $NaBD_4$: 350 (1), 282* (25), 206 (3), 207 (3), 192 (12), 167* (6), 147 (33), 118 (5), 105 (38), 93* (13) 73 (100)
12.3	$CH_2OH–CH_2OH–CH_2–CH{=}CH–CO_2H$ MW 362 $(CH_2OH–CO–CH_2–CH{=}CH–CO_2H$, $CHO–CO_2H$,  $CHO{-}CHOH{-}CHOH{-}\overset{O}{HC{-}CH}{-}CHO)$	$NaBH_4$: 347 (1), 259 (17), 230 (22), 205 (29), 147 (54), 133 (12), 117 (3), 103 (4), 97 (22) 73 (100), $NaBD_4$: 348 (3), 260 (24), 230 (35), 206 (33), 147 (63), 133 (14), 118 (32), 104 (3), 103 (3), 98 (22) 73 (100)
13.2	$CH_2OH–CHOH–CH{=}CH–CHOH–CH_2OH$ MW 436 $(CHO–CHOH–CH{=}CH–CO–CH_2OH$, $CHO–CO–CH{=}CH–CO–CH_2OH$, $CHO–CO–CH{=}CH–CO–CHO)$	$NaBH_4$: 346 (6), 333 (1), 243 (6), 231 (7), 205 (21), 147 (40), 142 (18), 117 (18), 103 (4), 73 (100), $NaBD_4$: 350 (2), 349 (3), 334 (2), 246 (4), 233 (8), 207 (12), 206 (28), 147 (66), 144 (22), 118 (12), 104 (2), 103 (5), 73 (100)
13.4, 13.7	$CH_2OH–CHOH–CHOH–CH{=}CH–CH_2OH$ MW 436 $(CHO–CHOH–CO–CH{=}CH–CHO)$	$NaBH_4$: 346 (3), 333 (4), 319 (8), 307 (5), 243 (16), 217 (7), 205 (6), 147 (44), 129 (58), 103 (14), 73 (100); $NaBD_4$: 349 (1), 336 (3), 321 (5), 309 (9), 246 (7), 245 (7), 219 (6), 206 (5), 147 (47), 131 (40) 104 (14), 73 (100)
13.9, 14.1	$CH_2OH–CHOH–CHOH–CHOH–CH_2OH$ MW 512 (contains at least two carbonyl functions, *e.g.* $CHO–CHO–CHOH–CHOH–CHO$)	$NaBH_4$: 319 (11), 307 (21), 217 (40), 205 (15) 147 (39), 129 (23), 103 (21), 73 (100); $NaBD_4$: 321 (3), 320 (2), 309 (3), 308 (3), 207 (5), 206 (8), 147 (51), 131 (31), 104 (13), 103 (9), 73 (100)
14.4, 14.6	Pentahydroxycyclohexane MW 524 (contains at least two carbonyl functions)	$NaBH_4$: 405 (2), 345 (4), 318 (28), 246 (18), 205 (5), 156 (13), 147 (40), 133 (10), 117 (14), 103 (4), 73 (100), $NaBD_4$: 407 (1), 346 (3), 319 (24), 247 (15), 206 (9), 157 (12), 147 (47), 133 (9), 118 (13), 103 (3), 73 (100)
14.7	$CH_2OH–CHOH–CHOH–CHOH–CO_2H$ MW 526 $CHO–CHOH–CHOH–CHOH–CO_2H$	$NaBH_4$: 333 (6), 307 (4), 292 (28), 217 (16), 205 (16), 189 (6), 147 (45), 117 (13), 103 (12), 73 (100); $NaBD_4$: 335 (2), 333 (4), 308 (2), 292 (28), 218 (13), 206 (15), 191 (4), 147 (15), 118 (10), 104 (9), 103 (9), 73 (100)
14.9, 15.2	$CH_2OH–CHOH–CH{=}CCl–CHOH–CH_2OH$ MW 470 $(CHO–CHOH–CH{=}CCl–CHOH–CHO$, $CH_2OH–CO–CH{=}CCl–CO–CH_2OH$, $CHO–CHOH–CH{=}CCl–CHO–CH_2OH)$	$NaBH_4$: 435 (< 1); 380* (1), 367* (5), 331 (5), 277* (23), 205 (18), 147 (47), 129 (10), 103 (23), 93* (4) 73 (100); $NaBD_4$: 382* (2), 370* (13), 369* (13), 368* (13), 333 (9), 332 (13), 280* (30), 279* (37), 278* (30), 207 (8), 206 (23), 147 (80), 104 (18), 103 (13), 93* (5), 73 (100)

[a] The carbonyl groups were reduced with either $NaBH_4$ or $NaBD_4$ and the resulting polyols trimethylsilylated. The chlorine-containing m/z signals are marked by an asterisk. The retention time (RT) refers to Fig. 3. Assignment of the tetrahydroboranate-reduced form are given first; inferred formulae of radiolysis products are given in parentheses. Isomers may show essentially identical mass spectra unless they are deuteriated differently. They are listed only once and their respective retention times are indicated together in column 1.

resulting alcohol function; this yields important information for the analysis of the mass spectra of their trimethylsilyl (TMS) ethers which are obtained upon rotary-evaporating the aqueous solutions, eliminating the boric acid with methanol–formic acid and trimethylsilylation of the residue.[12] The mass spectra are compiled in Table 2. Often a given polyhydric alcohol has more than one precursor, which leads to a somewhat complex deuteriation pattern. Hence, assignment is tentative in these cases, but nevertheless clearly shows the type of the precursor compounds. The fragmentation pattern of the trimethylsilylated open-chain polyhydric alcohols is usually relatively simple, and assignments are therefore straightforward,[12] but considerably less is known about the fragmentation patterns of the trimethylsilyl ethers of unsaturated and cyclic polyhydric alcohols. In most of the mass spectra the molecular ions and the $m/z = M^+ - 15$ are missing. However, the GC-retention times of the products follow a clear pattern which assists in the assignment; further, glycerol, the tetritols and pentitols, for which reference material is available, serve as benchmarks. Lacking confirmatory evidence from other techniques, *e.g.* NMR (which, short of chemical isolation of the products, are not applicable here owing to the large number of the products and their low concentrations), some of the assignments must remain tentative. This, however, does not affect the overall picture. For quantitation of these products, D-mannitol was used as an internal standard.

Results and discussion

The radical-generating system

Hydroxyl radicals were generated radiolytically in N_2O-saturated aqueous solutions [reactions (1) and (2)]. The radiation-chemical yields of the primary radicals are $G({}^{\bullet}OH) \approx G(e_{aq}^-) = 2.9 \times 10^{-7}$ mol J^{-1} and $G(H^{\bullet}) = 0.6 \times 10^{-7}$mol J^{-1}. Solvated electrons react with N_2O, yielding further ${}^{\bullet}OH$ radicals.[13] Both radicals react with chlorobenzene by addition to the ring [*e.g.* reactions (4)–(7), see below].

$$H_2O \xrightarrow[\text{radiation}]{\text{ionizing}} {}^{\bullet}OH, e_{aq}^-, H^{\bullet}, H^+, OH^-, H_2, H_2O_2 \qquad (1)$$

$$e_{aq}^- + N_2O \longrightarrow {}^{\bullet}OH + N_2 + OH^- \qquad (2)$$

In the presence of O_2, the H atoms are converted into $HO_2^{\bullet}$–$O_2^{\bullet -}$ radicals [reaction (3); $pK_a(HO)_2^{\bullet}) = 4.8$].

$$H^{\bullet} + O_2 \rightleftharpoons HO_2^{\bullet} \qquad (3)$$

The chlorobenzene OH-adduct radicals **1–3** react with O_2 reversibly to give the corresponding peroxyl radicals,[10] as will be discussed in more detail below.

Reactions in the absence of oxygen

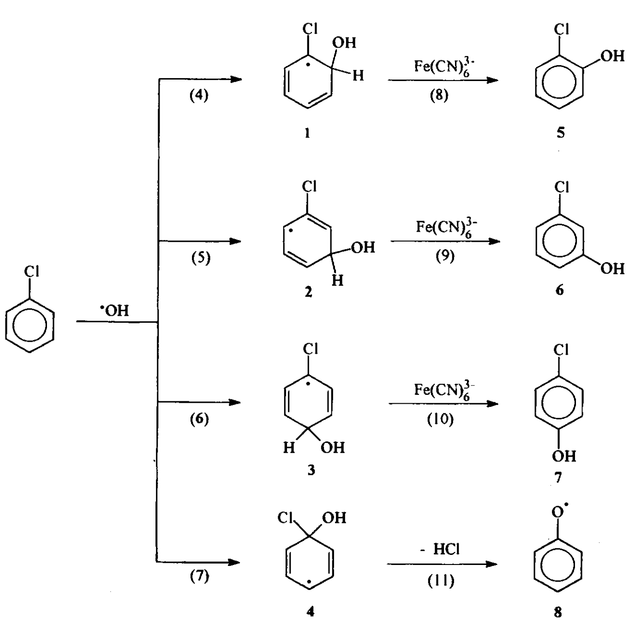
When ${}^{\bullet}OH$ radicals react with chlorobenzene, four different hydroxycyclohexadienyl-type radicals may be formed [radicals **1–4**; reactions (4)–(7); $k_{4-7} = 4.5 \times 10^9$ dm^3 mol^{-1} s^{-1}, *cf.* ref. 1] . The yield of **1–3** can be determined by their oxidation with $Fe(CN)_6^{3-}$ [reactions (8)–(10)].[9,14–20]

Table 3 *G* values (in units of 10^{-7} mol J^{-1}) of chlorophenol and chloride ion formation in the γ-radiolysis of chlorobenzene in aqueous solution, N_2O-saturated, N_2O-saturated in the presence of $Fe(CN)_6^{3-}$ and N_2O–O_2 (4 : 1)-saturated

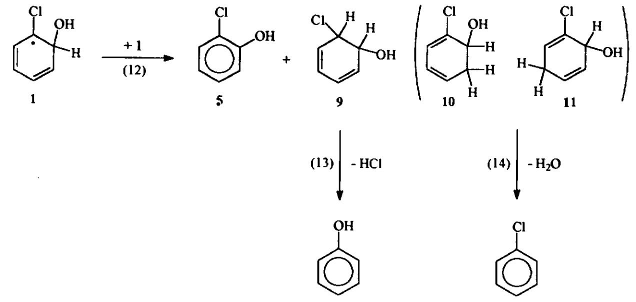
Products	N_2O	N_2O–$Fe(CN)_6^{3-}$	N_2O–O_2
2-Chlorophenol	0.15	2.5	0.7
3-Chlorophenol	0.10	1.25	0.5
4-Chlorophenol	0.15	1.75	0.9
Total chlorophenols	0.4	5.5	2.1
Chloride ion	1.0 (1.1)[a]	0.03[b] (0.2)[a]	3.3

[a] After heating at 60 °C for 1.5 h. [b] Immediate (from pulse radiolysis).

The radiation-chemical yields of the chlorophenols **5–7** formed under these conditions are compiled in Table 3. It can be seen from these data that their combined yield is very close to that of ${}^{\bullet}OH$ radicals in this system, *i.e.* there is only very little room for the *ipso*-addition [reaction (7)]. The *ipso*-OH-adduct **4** should rapidly eliminate HCl, thereby forming the phenoxyl radical **8** [reaction (11); *cf.* refs. 21–23]. This is confirmed by pulse radiolysis experiments (data not shown): there is practically no ($G < 0.03 \times 10^7$ mol J^{-1}) permanent conductivity increase on the fast timescale (< 50 ms) that could be ascribed to the formation of HCl from reaction (11), and there is also no significant absorption at 420 nm where the phenoxyl radical **8** has a strong absorption band ($\varepsilon = 2200$ dm^3 mol^{-1} cm^{-1}, *cf.* ref. 24). The *ortho*:*meta*:*para* ratio of the three chlorinated phenols is 1 : 0.5 : 0.7, but considering that there are two *ortho*- and *meta*-positions and one *para*-position, the probability of adding to the *para*-position is the highest (48%), followed by the *ortho*-position (35%), while the *meta*-position is the least likely to be attacked (17%). This observation is in line with the electrophilic nature of the ${}^{\bullet}OH$ radical. Obviously, steric effects also play a significant role, as is shown by the very low probability of the *ipso*-addition (< 1%).



The chlorohydroxycyclohexadienyl radicals **1–3** absorb strongly at 325 nm (overall $\varepsilon = 4600$ dm^3 mol^{-1} cm^{-1}) as is typical[10] for such radicals. In their bimolecular decay ($2k = 1.9 \times 10^9$ dm^3 mol^{-1} s^{-1}, measured pulse-radiolytically by following the decay at 325 nm, data not shown), a small percentage of the radicals disproportionate, leading to the formation of the chlorinated phenols **5–7** [*e.g.* reaction (12)] and chlorohydroxycyclohexadienes (*e.g.* **9–11**) which may either eliminate HCl yielding phenol [*e.g.* reaction (13)] or eliminate water, thereby reverting to chlorophenol [*e.g.* reaction (14)].



The rate of these reactions, especially the water elimination, does not seem to be very fast, considering that chlorohydroxycyclohexadiene structures are preserved in some of the dimers for a prolonged period of time (see below). As can be seen from Table 1, the chlorophenol yields are low, *i.e.* disproportionation reactions are of minor importance (*ca.* 14%). This is similar to the behaviour of other hydroxycyclohexadienyl radicals.[9,10] Since *G*(phenol) is less than 0.1×10^7 mol J^{-1}, it is clear that reactions such as (12) followed by (13) do not contribute significantly to product formation.

In competition with the disproportionation, the radicals **1–3** dimerize [*e.g.* reactions (15) and (16)]. In these reactions $R^{\bullet}$ denotes any of the radicals **1–3**. The resulting products are

Table 4 G values (in units of 10^{-7} mol J^{-1} related to the monomer units) of dimeric products in the γ-radiolysis of N_2O-saturated aqueous solution of chlorobenzene (10^{-3} mol dm^{-3}) immediately after irradiation and after heating the samples at 65 °C for 1.5 h at pH 1

Product	Prompt	After heating
x,*x*′-Dichlorobiphenyls	0.35	2.1
x-Chloro-*x*′-hydroxybiphenyls	0.35	1.2
x-Chloro-*y*-hydroxycyclohexadienylchlorobenzenes	1.8	0.25
x,*x*′-Dihydroxybiphenyls	0.2	0.35
x-Chloro-*y*-hydroxycyclohexadienylphenols	2.2	absent

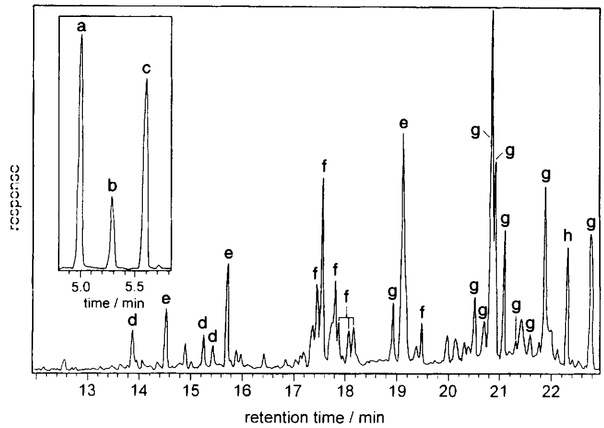


Fig. 1 γ-Radiolyis of N_2O-saturated aqueous solutions of chlorobenzene (10^{-3} mol dm^{-3}). Gas chromatogram of a trimethylsilylated diethyl ether extract. Assignments: **a**: 2-chlorophenol, **b**: 3-chlorophenol, **c**: 4-chlorophenol, **d**: *x*,*x*′-dichlorobiphenyls, **e**: *x*-chloro-*y*-hydroxybiphenyls, **f**: *x*-chloro-*y*-hydroxycyclohexadienylchlorobenzenes, **g**: *x*-chloro-*y*-hydroxycyclohexadienylphenols, **h**: *x*,*x*′-dihydroxybiphenyls (RT = 22.3 min for 4,4′-dihydroxybiphenyl).

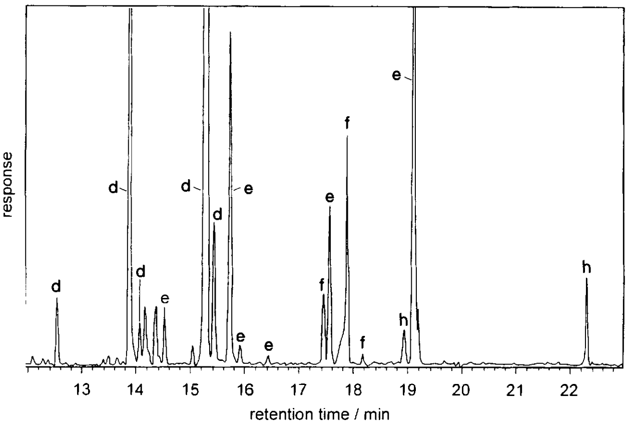
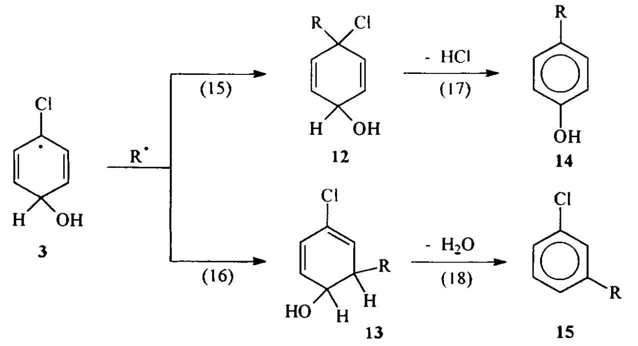


Fig. 2 γ-Radiolyis of N_2O-saturated aqueous solutions of chlorobenzene (10^{-3} mol dm^{-3}) followed by 1.5 h heating at pH 1. Gas chromatogram of a trimethylsilylated diethyl ether extract. Assignments as in Fig. 1.

bis(chlorohydroxycyclohexadienes). Fig. 1 shows a gas chromatogram of a sample which has been extracted with diethyl ether immediately after irradiation (1.5 h) and subjected to GC–MS analysis after trimethylsilylation. Six classes of compounds are recognized which result from the ˙OH radical reactions: the chlorinated phenols (**a**–**c**, Inset in Fig. 1), *x*,*x*′-dichlorobiphenyls (**d** in Fig. 1), *x*-chloro-*x*′-hydroxybiphenyls (**e**), *x*-chloro-*y*-hydroxycyclohexadienylchlorobenzenes (**f**), *x*-chloro-*y*-hydroxycyclohexadienylphenols (**g**), and *x*,*x*′-dihydroxybiphenyls (**h**). The minor primary radical in this system, the H atom, gives rise to chlorocyclohexadienyl radicals which mainly interact with the major radicals, the OH-adducts **1**–**3**. Chlorobiphenyl is one of the resulting products (eluting at 11.7 min, not shown in Fig. 1), but there are also some other minor unidentified products which may be due to this precursor. Typical mass spectra are compiled in Table 1. After heating the irradiated solution at pH 1 for 1.5 h prior to extraction, most of the chlorohydroxycyclohexadienyl structures are converted either into a phenolic or a chlorophenylic function [*cf.* reactions (17) and (18)], except for three isomers which retain the chlorohydroxycyclohexadienyl structure (*cf.* Figs. 1 and 2, Table 4).



When the radicals **1** and **3** combine at the *ipso*-position of the chlorine substitutent, they can, through HCl elimination, give rise to dihydroxybiphenyls [*cf.* reaction (17)]. Of the three conceivable isomers, only two are observed, 4,4′-dihydroxybiphenyl (type **14**) and in a much lower yield an isomer which we suggest to be 2,4′-dihydroxybiphenyl. A considerable steric hindrance at the *ipso*-position in the case of an adjacent–C(H, OH)-group may lead to a lower probability for crosslinking at this position. This would also explain the absence of the third isomer (2,2′-dihydroxybiphenyl) whose yield would be too low for detection.

After heating G(chloride ion) = 1.1 × 10^{-7} mol J^{-1} is found, *i.e.* only 19% of the chlorine is labile and eliminated eventually.

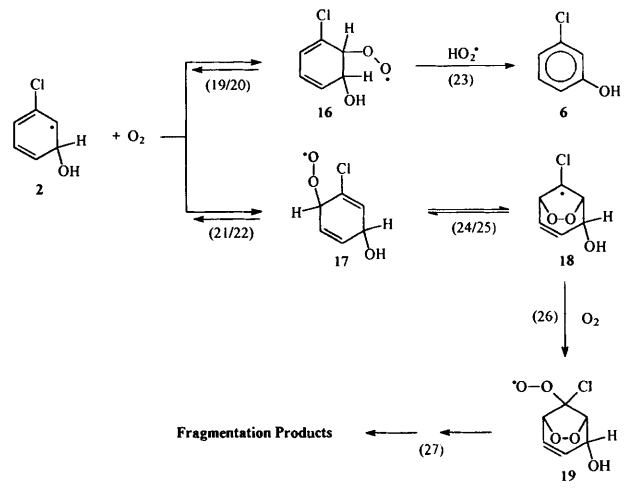
Reactions in the presence of oxygen

In contrast to most other carbon-centred radicals, which at room temperature react with O_2 irreversibly and at close to diffusion-controlled rates to give the corresponding peroxyl radicals,[25,26] the reaction of hydroxycyclohexadienyl radicals with O_2 is much slower, besides being reversible, both in aqueous solution[7,8,10,20,26] and in the gas phase.[27] For the present system, the situation is illustrated by reactions (19)–(22).

Since there are three different hydroxycyclohexadienyl radicals (**1**–**3**) in this system, each will have its own rate constant for O_2 addition [*cf.* reactions (19) and (21)], and each of their corresponding peroxyl radicals its own rate constant for O_2 elimination [*cf.* reactions (20) and (22); structures **16** and **17** each represent two stereoisomers]. Nevertheless, following a recent study,[10] it is possible to characterize the system by overall rate constants k_{forward} (O_2 addition) and k_{reverse} (O_2 elimination). These rate constants (which imply a stability constant) and the overall rate constant of the subsequent unimolecular decay according to reactions such as (23) and

Table 5 Rate constants of the reactions pertinent to the present study

Reaction	Rate constant	Ref.
$^{\bullet}OH$ + chlorobenzene→**1,2,3**	5.5×10^9 dm^3 mol^{-1} s^{-1}	1
2 (**1,2,3**)→Products	1.9×10^9 dm^3 mol^{-1} s^{-1}	This work
(**1,2,3**) + O_2→$RO_2^{\bullet}$, *e.g.* **16,17**	2.6×10^8 dm^3 mol^{-1} s^{-1}	10
$RO_2^{\bullet}$ (*e.g.* **16,17**)→(**1, 2,3**) + O_2	5.5×10^4 s^{-1}	10
$RO_2^{\bullet}$ (*e.g.* **16, 17**)→Products	1.1×10^3 s^{-1}	10



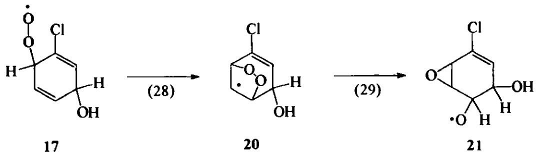
(24)–(27), have been measured in the course of the present study. These rate constants are compiled in Table 5. They are also tabulated amongst the material given in ref. 10.

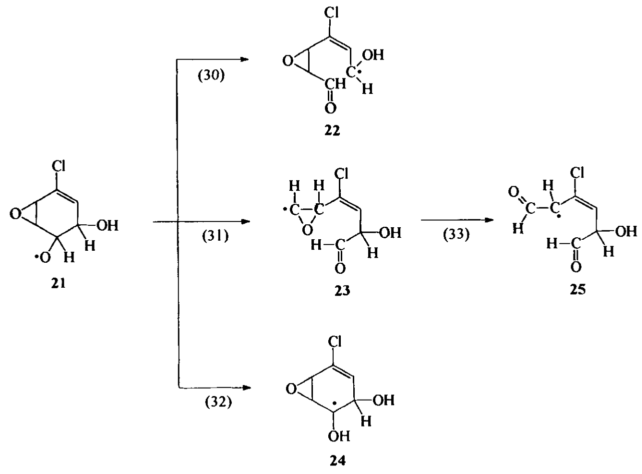
The chlorinated phenols **5–7** are formed from radicals of the type **16** in an $HO_2^{\bullet}$ elimination [*cf.* reaction (23)]. Owing to the possibility of allylperoxyl rearrangement in these systems, the various cyclohexadienylperoxyl species may interconvert,[28–30] and the phenols **5–7** may lack a definite peroxyl precursor. The yields of the phenols are considerably below those observed when $Fe(CN)_6^{3-}$ is used as an oxidant (see Table 3). The reason for this is thought to be competition between $HO_2^{\bullet}$ elimination [*cf.* reaction (23)] and a cyclization reaction [*cf.* equilibrium (24/25)] followed by a rapid addition of O_2 [reaction (26)] which fixes the *endo*-peroxidic structure. A more detailed discussion of this situation is found in ref. 8. Although the hypothesis of *endo*-peroxide formation disagrees with certain findings reported for other allylperoxyl systems (*e.g.* refs. 29–31), it receives some support from other published work relating to the gas phase.[32,33] Interestingly, the formation of the 1,2-dioxolan-4-yl structure from allyl and O_2 has been computed to be exothermic by 93 kJ mol^{-1}.[33] In any case, it is hard to see how to explain (*i*) the extensive ring fragmentation (Tables 2 and 6) and (*ii*) the considerable degree of removal of C=C unsaturation found in the fragmentation products without the intermediacy of this structure. In particular, the route *via* hydroxycyclohexadienyloxyl $>CH–O^{\bullet}$ (from 2 $>CH–OO^{\bullet}\rightarrow 2$ $>CH–O^{\bullet}$ + O_2) appear unsuitable. Water-catalysed rearrangement[34–37] $>CHO^{\bullet}\rightarrow>C(OH)^{\bullet}$ with subsequent O_2 addition and superoxide elimination[26] would ultimately (after rearomatization) result in hydroxyphenolic compounds, while β-fragmentation of an oxyl radical would eventually produce hexadienyl-type products, an option which is, however, open only to those that possess the β–γ C–C single bond structure element, as can be shown.

Intramolecular epoxide formation undergone by radicals in the β-position to a peroxidic function such as **18** and **20** (*cf.* refs. 38,39 and refs. cited therein) may represent a further conceivable pathway to fragmentation products [*e.g.* reactions (28) and (29), and subsequent reactions (30)–(31), (33)]. These reactions must compete with the fixation of the *endo*-peroxidic radical by oxygen [*e.g.* reaction (26)]. The epoxide pathway can only be effective if the rate of reaction such as (29) is sufficiently fast. The rate constants for this type of reaction seem to vary considerably (values between 10^2 and near 10^6 s^{-1} have been reported).[38,39] From the fast rate of O_2 addition at ambient O_2 concentrations [reaction (26)] it follows that the rate constants of epoxide-forming reactions, such as reaction (29), must be in the upper range of the reported spread to enable the epoxide pathway.

Table 6 γ-Radiolysis of chlorobenzene in $N_2O–O_2$ (4:1)-saturated aqueous solutions. *G* values (in units of 10^{-7} mol J^{-1}) of the fragment products (carbonyl compounds are given in their reduced form; for assignments see Table 2)

Product	*G* Value
HCO_2H	2.5
$CHO–CO_2H$	0.1
$CH_2OH–CO_2H$	0.1
Cl-free compounds containing 2 carbon atoms	0.3
Cl-free compounds containing 3 carbon atoms	0.8
Cl-free compounds containing 4 carbon atoms	1.0
Cl-free compounds containing 5 carbon atoms	1.0
Cl-free compounds containing 6 carbon atoms	0.35
CHO–CH=CCl–CHO	<0.1
CHO–CH=CCl–CO–CHO	<0.1
$CO_2H–CH_2–CH=CCl–CO–CHO$	<0.1
CHO–CHOH–CH=CCl–CHOH–CHO, $CH_2OH–CO–CH=CCl–CO–CH_2OH$, $CHO–CHOH–CH=CCl–CO–CH_2OH$	0.25





As a consequence of the bimolecular decay of the *endo*-peroxide-derived peroxyl radical **19** and the other peroxyl radicals, the six-membered ring is cleaved and fragmention products are formed [*cf.* reaction (27) and/or (30) and (31)] that may contain one or more carbonyl functions.

The gas chromatogram (Fig. 3) obtained upon reduction of the sample by $NaBH_4$ or $NaBD_4$ and trimethylsilylation reveals that a large number of such fragmentation products are formed. Fig. 3 also gives an impression of the relative importance of the various fragmentation products. The mass spectra are given in Table 2. The assignment of the products is discussed in the Experimental section. *G* values are compiled in Table 6. It can be seen from Table 2 that the majority of the fragmentation products no longer contain chlorine. In accordance with this, a large part of the chlorine shows up as chloride ion (see Table 3). In addition to chloro-3,6-dihydroxycyclohexa-1,4-diene there are a few open-chain chlorinated products such as CHO–CH=CCl–CHO, CHO–CH=CCl–CO–CHO and espec-

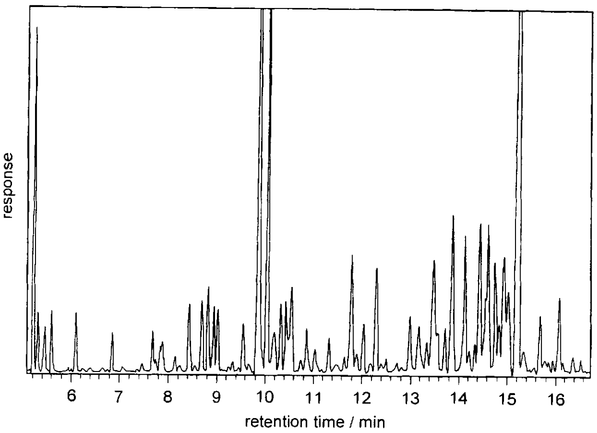


Fig. 3 γ-Radiolyis of N_2O–O_2 (4:1)-saturated aqueous solutions of chlorobenzene (10^{-3} mol dm^{-3}). Gas chromatogram of a $NaBH_4$-reduced and trimethylsilylated sample.

ially products of the type CH_2OH–CO–CH=CCl–CO–CH_2-OH that are produced in low yields. All of these contain vinylic chlorine.

The foregoing are primary products which are still far from the desired state of complete mineralization; as Table 3 indicates, about half of the organic chlorine has been converted into chloride. Regarding the system from the water-purification point of view, it can be said that monochloro-substituted alkenic compounds and the chlorinated phenols react quite readily with ozone [*e.g.* $k(O_3 + CH_2{=}CHCl) = 2.4 \times 10^4$ dm^3 mol^{-1} s^{-1};[40] $k(O_3 +$ 2-chlorophenol$) = 1.1 \times 10^3$ dm^3 mol^{-1} s^{-1}; $k(O_3 +$ 4-chlorophenol$) = 6 \times 10^2$ dm^3 mol^{-1} s^{-1}, *cf.* ref. 6], and hence there is good reason to expect that when the $^{\bullet}OH$ radicals are generated in an ozone-based water purification process (such as O_3–H_2O_2) these oxidation products may become further degraded.

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