Oxidation of benzyl radicals by $Fe(CN)_6{}^{3-}$

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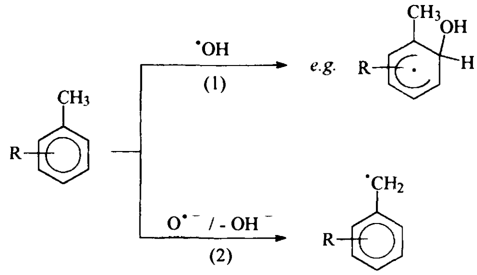
Hydroxyl radicals and their anions [$O^{\bullet-}$ radicals, $pK_a(^{\bullet}OH) = 11.9$] have been generated radiolytically in N_2O-saturated aqueous solution and reacted with 4-chlorotoluene. While the $^{\bullet}OH$ radical mainly produces hydroxycyclohexadienyl-type radicals, the $O^{\bullet-}$ radical practically only abstracts H atoms from the methyl group yielding 4-chlorobenzyl radicals ($k = 1.9 \times 10^9$ dm^3 mol^{-1} s^{-1}; determined by pulse radiolysis). The radicals formed by $^{\bullet}OH$ radical attack at pH 7 (mainly hydroxycyclohexadienyl-type radicals) are oxidized by $Fe(CN)_6{}^{3-}$ ($k = 1.8 \times 10^7$ dm^3 mol^{-1} s^{-1}) giving rise to the following products (G values in units of 10^{-7} mol J^{-1} are given in parentheses): 4-chloro-2-hydroxytoluene (2.9), 4-chloro-3-hydroxytoluene (2.4), 4-chlorobenzyl alcohol (0.05), 4-chlorobenzaldehyde (0.1) and 4-chloro-2-hydroxybenzaldehyde (0.15). The 4-chlorobenzyl radical is the main species formed at pH 13.7 and is oxidized by $Fe(CN)_6{}^{3-}$ with a similar rate constant ($k = 4.2 \times 10^7$ dm^3 mol^{-1} s^{-1}), the major products being 4-chlorobenzaldehyde (3.7), 4-chloro-2-hydroxybenzaldehyde (0.65) and 4-chlorobenzyl alcohol (0.5). From $^{\bullet}OH$ radical attack (*ca.* 10% at this pH), 4-chloro-2-hydroxytoluene (0.4) and 4-chloro-3-hydroxytoluene (0.3) are also formed. It is suggested that the oxidation of the 4-chlorobenzyl radical by $Fe(CN)_6{}^{3-}$ yields in the first step a carbocation which cyclizes by deprotonation. The resulting cyclohexadienyl-type radical undergoes β-fragmentation yielding the 4-chlorobenzyloxyl radical. A 1,2-H shift and subsequent oxidation leads to 4-chlorobenzaldehyde. The unsubstituted benzyl radical is also oxidized by $Fe(CN)_6{}^{3-}$ yielding benzaldehyde in high yields.

Introduction

Hydroxyl radicals are known to react with toluene and its derivatives by mainly adding to the ring [formation of hydroxycyclohexadienyl-type radicals, reaction (1)], while its basic form, the $O^{\bullet-}$ radical [$pK_a(^{\bullet}OH) = 11.9$],[1] predominantly abstracts an H atom from the methyl group to form benzyl-type radicals [reaction (2)].[2,3]



Hydroxycyclohexadienyl-type radicals can be oxidized by $Fe(CN)_6{}^{3-}$ thereby yielding the corresponding phenols.[4–9] The rate constants of these reactions depend on the nature of substituents present. Electron-withdrawing substituents reduce the rate of oxidation[8] and under unfavourable conditions the oxidative power of $Fe(CN)_6{}^{3-}$ might not be sufficient to complete the oxidation in competition with bimolecular termination reactions. $IrCl_6{}^{2-}$ might then be the oxidant of choice.[10]

Much less is known about the oxidation of benzyl radicals by $Fe(CN)_6{}^{3-}$. When the unsubstituted benzyl radical reacted with Fe^{III} ions at pH 3, oxidation of the benzyl radicals was only partial, but besides benzyl alcohol noticeable amounts of benzaldehyde were formed.[11] In contrast, the oxidation of the 4-chlorobenzyl radical by $Fe(CN)_6{}^{3-}$ seemed to be quantitative, the major product being 4-chlorobenzaldehyde with minor amounts of 4-chlorobenzyl alcohol.[12]

This is a surprising observation, because 4-chlorobenzyl alcohol is not oxidized under such conditions. Thus, the oxidation of the 4-chlorobenzyl radical by the one-electron oxidant $Fe(CN)_6{}^{3-}$ to 4-chlorobenzaldehyde, a three-electron oxidation process, cannot involve the one-electron oxidation product, 4-chlorobenzyl alcohol, as an intermediate. We felt that this puzzling observation deserved a more detailed study.

Experimental

4-Chlorotoluene, toluene, benzaldehyde, 4-chlorobenzyl alcohol and 4-chloro-3-hydroxytoluene (Merck) and 4-chlorobenzaldehyde (Fluka) were used without further purification. Solutions were made up in Milli-Q (Millipore) filtered water. γ-Irradiations were carried out in a ^{60}Co Panorama γ-source (Nuclear Engineering) at a dose rate of 0.18 Gy s^{-1}, which was determined by Fricke dosimetry. The pulse radiolysis set-up has been described previously.[13]

For their identification the radiation products were extracted from the aqueous solutions into diethyl ether with a Ludwig extractor (Normag). After drying (Na_2SO_4) the diethyl ether extract was concentrated, the residue trimethylsilylated with *N*,*N*-bis(trimethylsilyl)trifluoroacetamide (BSTFA; Macherey Nagel) to convert phenols into their trimethylsilyl ethers and analysed by gas chromatography–mass spectrometry (Hewlett-Packard 5971A mass selective detector coupled with an HP 5890 Series II gas chromatograph), 12 m × 0.2 mm HP-Ultra 1 (crosslinked silicone gum) column, temperature programmed, 60–270 °C. The mass spectra of the products are characterized by their most abundant *m*/*z* (the chlorine-containing ions are indicated with an asterisk): 4-chlorobenzaldehyde (MW = 140): 50 (27%), 75 (38), 111 (60), 139 (100)* and 140 (77)*; 4-chloro-2-hydroxytoluene–TMS (MW = 214): 73 (15%), 93 (58), 105 (26), 163 (81), 199 (100)* and 214 (40)*; 4-chloro-3-hydroxytoluene–TMS (MW = 214): 73 (23%), 93 (18), 125 (34), 163 (10), 199 (100)* and 214 (45)*; 4-chlorobenzyl alcohol–TMS (MW = 214): 73 (7%), 93 (7), 125 (100), 169 (21), 179 (18), 199 (49)* and 214 (4)*; 4-chloro-2-hydroxybenzaldehyde–TMS (MW = 228): 75 (13%), 111 (37), 139 (69)*, 169 (46), 213 (100)* and 228 (5)*.

Quantification of the products was carried out with high performance liquid chromatography (HPLC). Separation of the products was achieved on a 25 cm Nucleosil C-18 column (Merck) using 60% methanol containing 2 × 10^{-4} mol dm^{-3} KH_2PO_4 as eluent. Under this condition 4-chlorobenzaldehyde and 4-chloro-3-hydroxytoluene were not fully separated. However, the aldehyde can be derivatized by methoxyamine (SERVA) into the corresponding methoxime which is well separated from the other products.

For quantification of the 4-chloro-3-hydroxytoluene by HPLC, reference material was available. In order to arrive at the yield of the other isomer, 4-chloro-2-hydroxytoluene, the trimethylsilylated diethyl ether extracts were gas chromatographed and their relative yields determined by flame ionization detection. Since these two isomers must have the same response factor the yield of 4-chloro-2-hydroxytoluene can be based on this ratio and the yield of 4-chloro-3-hydroxytoluene. The yield of 4-chloro-2-hydroxybenzaldehyde was estimated assuming the same response factor as 4-chloro-2-hydroxytoluene. This will result in only a minor underestimate of its yield.

In the γ-radiolysis of 4-chlorobenzyl alcohol (1 × 10^{-3} mol dm^{-3}) at pH 7 and in the presence of $Fe(CN)_6{}^{3-}$ (10^{-3} mol dm^{-3}) 4-chloro-2-hydroxybenzyl alcohol and 4-chloro-3-hydroxybenzyl alcohol were observed as major products. The mass spectra of their di-TMS-derivatives (MW = 302) are characterized by their most abundant *m*/*z*: 73 (100%), 147 (31), 169 (12), 179 (13), 199 (12), 213 (26)*, 267 (48), 287 (30)*, 302 (22)* and 73 (55), 93 (28)*, 147 (9), 179 (17), 197 (16), 213 (100)*, 257 (31), 267 (51), 287 (49)* and 302 (39)*, respectively. The isomer represented by the first mass spectrum is the more abundant product and since in the case of 4-chlorotoluene $^{\bullet}$OH addition to the 2-position is favoured over the addition to the 3-position, we suggest that it is the di-TMS ether of 4-chloro-2-hydroxybenzyl alcohol. The second mass spectrum represents the 4-chloro-3-hydroxybenzyl alcohol.

After the γ-radiolysis of N_2O-saturated 2 × 10^{-3} mol dm^{-3} dimethyl sulfoxide in the presence of 10^{-3} mol dm^{-3} $Fe(CN)_6{}^{3-}$ the formation of formaldehyde was checked after derivatizing the aldehyde with pentafluorobenzyl hydroxylamine using GC–MS with single-ion monitoring (m/z = 225, M^+) and relating its signal to an internal standard (the corresponding cyclohexanone derivative; m/z = 293, M^+).

The consumption of $Fe(CN)_6{}^{3-}$ has been measured spectrophotometrically at 420 nm. As is typical for the determination of *G*(consumption) values, such values are fraught with a considerable error (25% may be a reasonable estimate).

Results and discussion

The radical-generating system

Hydroxyl radicals and $O^{\bullet -}$ radicals were generated radiolytically in N_2O-saturated aqueous solutions at pH 7 and 13.7, respectively [reactions (3)–(6)].[14]

$$H_2O \xrightarrow[\text{radiation}]{\text{ionizing}} {}^{\bullet}OH, e_{aq}^{-}, {}^{\bullet}H, H^+, H_2O_2, H_2 \qquad (3)$$

$$e_{aq}^{-} + N_2O \longrightarrow {}^{\bullet}OH + N_2 + OH^- \qquad (4)$$

$${}^{\bullet}H + OH^- \longrightarrow e_{aq}^{-} \qquad (5)$$

$${}^{\bullet}OH \rightleftharpoons O^{\bullet -} + H^+ \qquad (6)$$

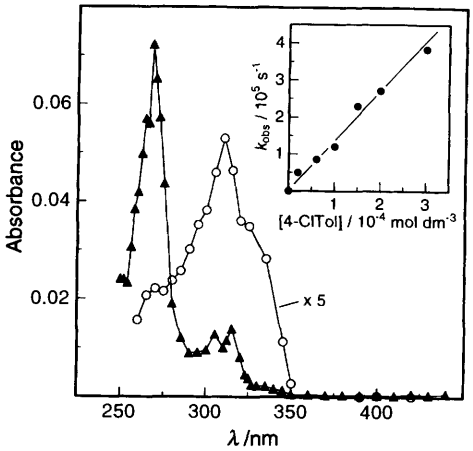


Fig. 1 Pulse radiolysis of N_2O-saturated aqueous solutions of 4-chlorotoluene (1 × 10^{-3} mol dm^{-3}). UV absorption spectra of the intermediates from the reactions of $^{\bullet}$OH radicals (○, pH 7, mainly OH-adduct radicals) and $O^{\bullet -}$ radicals (▲, pH 13.7, mainly 4-chlorobenzyl radicals). Inset: rate of formation of 4-chlorobenzyl radicals monitored at 268 nm as a function of the 4-chlorotoluene concentration.

The radiation chemical yields of primary radicals are $G(^{\bullet}OH) \approx G(e_{aq}^{-}) = 2.9 \times 10^{-7}$ mol J^{-1} and $G(^{\bullet}H) = 0.6 \times 10^{-7}$ mol J^{-1}. Solvated electrons react with N_2O yielding $^{\bullet}$OH radicals. In basic solutions, the H atoms are converted into solvated electrons [reaction (5)] and *via* reaction (4) give rise to further $^{\bullet}$OH radicals. Thus in neutral solutions $^{\bullet}$OH radicals are formed with $G(^{\bullet}OH) = 5.8 \times 10^{-7}$ mol J^{-1}, while at pH 13.7 [reaction (6)] $G(O^{\bullet -}) = 6.4 \times 10^{-7}$ mol J^{-1}. Both radicals react with added 4-chlorotoluene [reactions (7) and (8)].

$${}^{\bullet}OH + \text{4-chlorotoluene} \longrightarrow \text{product} \qquad (7)$$

$$O^{\bullet -} + \text{4-chlorotoluene} \longrightarrow \text{product} \qquad (8)$$

At pH 7 the $^{\bullet}$OH radicals mainly add to the ring ($k_7 = 5.5 \times 10^9$ dm^3 mol^{-1} s^{-1})[11] giving rise to hydroxycyclohexadienyl radicals. Such radicals typically have absorption maxima at *ca.* 310 nm and molar absorption coefficients[11,15] of *ca.* 4000 dm^3 mol^{-1} cm^{-1} and the UV spectrum given in Fig. 1 is in agreement with this general feature. In the absence of any additive, these radicals decay by clean second-order kinetics: when the inverse of the first half-life is plotted as a function of the dose per pulse a straight line going through the origin is obtained (data not shown), from which a bimolecular rate constant of $2k = 1.4 \times 10^9$ dm^3 mol^{-1} s^{-1} is obtained.

At pH 13.7, where the $O^{\bullet -}$ radical predominates, mainly H-abstraction from the methyl group occurs and the spectrum given in Fig. 1 is very close (formation of other radicals is minor, see below) to that of the 4-chlorobenzyl radical. It is characterized by a sharp maximum at 268 nm.[16] According to our measurements its molar absorption coefficient is 2 × 10^4 dm^3 mol^{-1} cm^{-1}, in good agreement with the similarly high values of other benzyl-type radicals.[2,3] The rate constant for reaction (8) has been determined to be $k_8 = 1.8 \times 10^9$ dm^3 mol^{-1} s^{-1} by measuring the build-up kinetics at 268 nm as a function of the 4-chlorotoluene concentration (inset in Fig. 1). The rate constant for the bimolecular decay of the 4-chlorobenzyl radicals has been measured at 2.1 × 10^9 dm^3 mol^{-1} s^{-1} (as described above). For a compilation of rate constants see Table 1.

Oxidation of the 4-chlorotoluene-derived radicals by $Fe(CN)_6{}^{3-}$

In the presence of $Fe(CN)_6{}^{3-}$ the 4-chlorotoluene-derived radicals are oxidized. The rate constant for this oxidation has been measured by pulse radiolysis by following the decay of the

Table 1 Compilation of rate constants measured in the present study

Reaction	$k/\mathrm{dm^3\ mol^{-1}\ s^{-1}}$
$O^{\cdot -}$ + 4-chlorotoluene	1.9×10^9
Bimolecular decay of 4-chlorotoluene–OH-adduct radicals	1.4×10^9
Bimolecular decay of 4-chlorobenzyl radicals	2.1×10^9
$Fe(CN)_6^{3-}$ + 4-chlorotoluene–OH-adduct radicals	1.8×10^7
$Fe(CN)_6^{3-}$ + 4-chlorobenzyl radicals	4.2×10^7

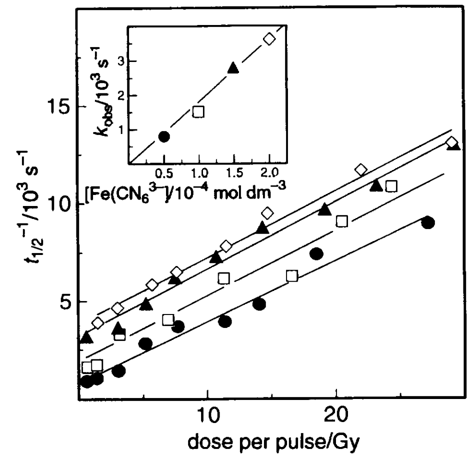


Fig. 2 Pulse radiolysis of N_2O-saturated aqueous solution of 4-chlorotoluene (1×10^{-3} mol dm^{-3}) containing varying amounts of $Fe(CN)_6^{3-}$. Inverse of the first half-life of the decay of $Fe(CN)_6^{3-}$ at 420 nm plotted as a function of dose per pulse. Inset: plot of k_{obs} (obtained from intercepts) *vs.* $[Fe(CN)_6^{3-}]$.

$Fe(CN)_6^{3-}$ absorption at 420 nm as a function of time after the pulse. The oxidation of the 4-chlorotoluene ·OH adduct radicals and the 4-chlorobenzyl radicals by $Fe(CN)_6^{3-}$ is not very fast. Thus in a pulse radiolytic experiment some bimolecular decay of the OH-adduct radicals (4-chlorobenzyl radicals) always occurs in competition with the oxidation process. In Fig. 2 the inverse of the first half-life of the decay at 420 nm is plotted as a function of the dose per pulse for different $Fe(CN)_6^{3-}$ concentrations at pH 7, [reaction of the 4-chlorotoluene OH-adduct radicals with $Fe(CN)_6^{3-}$]. An extrapolation to zero dose yields the inverse of the half-life of the first-order component, *i.e.* the oxidation process. In the inset of Fig. 2, k_{obs} obtained from the intercepts is plotted against the $Fe(CN)_6^{3-}$ concentration. From the slope a rate constant of $k_9 = 1.8 \times 10^7$ dm^3 mol^{-1} s^{-1} is obtained.

Similar experiments have been carried out at pH 13.7 (data not shown). From these data it is calculated that the 4-chlorobenzyl radical is oxidized by $Fe(CN)_6^{3-}$ with a rate constant of $k_{15} = 4.2 \times 10^7$ dm^3 mol^{-1} s^{-1}. Thus these radicals react with $Fe(CN)_6^{3-}$ with very similar rate constants.

On the pulse radiolysis timescale (using low doses per pulse) $G[Fe(CN)_6^{3-}$ consumption$] \approx 6 \times 10^{-7}$ mol J^{-1} matches approximately G(4-chlorobenzyl radicals). From the larger value of 12×10^{-7} mol J^{-1} for $G[Fe(CN)_6^{3-}$ consumption$]$ obtained after γ-radiolysis (Table 2) it is evident that there must be slower oxidation processes following the initial reaction to account for the excess. To follow these processes samples γ-irradiated at a dose rate of 2.8 Gy s^{-1} were rapidly transferred to the spectrophotometer for measurements. The irradiation time was 30 s and the transfer time 1.5 min. Thus a total of 2 min elapsed before the measurements could be started. The $Fe(CN)_6^{3-}$ decay after this period is shown in Fig. 3.

As can be seen from this figure, there is a considerable post-irradiation consumption of $Fe(CN)_6^{3-}$. This is much faster than the very slow intrinsic degradation of $Fe(CN)_6^{3-}$ at this pH in the presence of 4-chlorotoluene. This small contribution has been subtracted in Fig. 3 to show more clearly the post-irradiation effect.

Table 2 Products and G-values from the γ-radiolysis of N_2O-saturated solution of 4-chlorotoluene (10^{-3} mol dm^{-3}) in the presence of $Fe(CN)_6^{3-}$ (8×10^{-4} mol dm^{-3}) at pH 7 and 13.7. The values in brackets are yields per ·OH–$O^{\cdot -}$ (%)

	$G/10^{-7}$ mol J^{-1}	
Product	pH 7	pH 13.7
4-Chloro-2-hydroxytoluene	2.9 (50)	0.4 (6.5)
4-Chloro-3-hydroxytoluene	2.4 (42)	0.32 (5)
4-Chlorobenzyl alcohol	0.05 (1)	0.5 (8)
4-Chlorobenzaldehyde	0.1 (1.5)	3.7 (58)
4-Chloro-2-hydroxybenzaldehyde	0.15 (2.5)	0.65 (10.2)
Spontaneous HCl	0.18 (3)	n.d.
$Fe(CN)_6^{3-}$ consumption	5.6	12

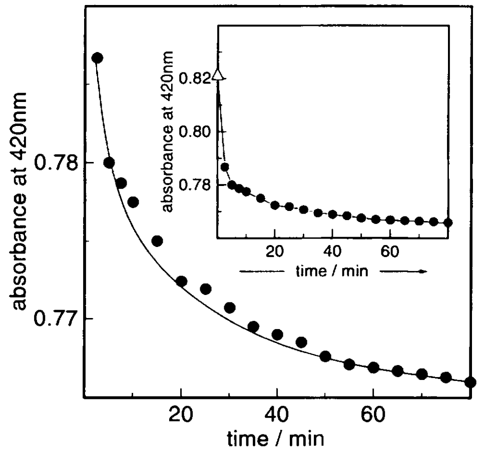


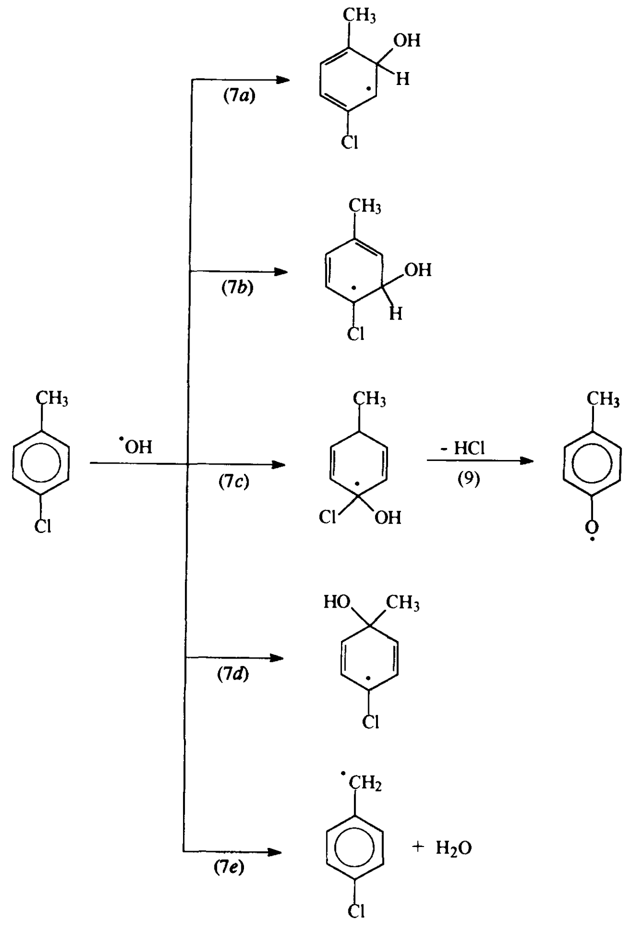
Fig. 3 γ-Radiolysis of an N_2O-saturated aqueous solution of 4-chlorotoluene (1×10^{-3} mol dm^3) at pH = 13.7 at a dose rate of 2.8 Gy s^{-1} for 0.5 min. Reduction of $Fe(CN)_6^{3-}$ (followed at 420 nm) as a function of time starting 2 min after irradiation. Corrections have been made for the small consumption of $Fe(CN)_6^{3-}$ with time of an unirradiated solution. Inset: the same data, but the absorbance of $Fe(CN)_6^{3-}$ before irradiation (△) is included.

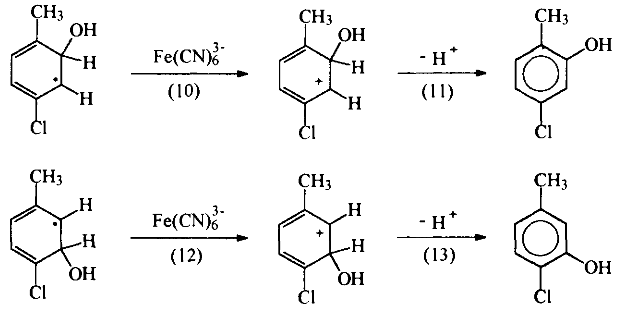
In a separate experiment $Fe(CN)_6^{3-}$ reacted with 4-chlorobenzyl alcohol under the same conditions (pH and temperature). Formation of 4-chlorobenzaldehyde was not observed over the time period of interest. Only upon heating such samples did the oxidation attain some significance. This is in agreement with the earlier conclusion[12] and our present data that 4-chlorobenzaldehyde is not formed upon oxidation of the primary (one-electron oxidized) product, 4-chlorobenzyl alcohol. Since $Fe(CN)_6^{3-}$ can only act as a one-electron oxidant, one has to look for other potential intermediates. This aspect will be discussed below.

Products from ·OH radical reactions; oxidation of the OH-adduct radicals by $Fe(CN)_6^{3-}$

The ·OH radicals will react with 4-chlorotoluene mainly by adding to positions which are not blocked by the CH_3 and Cl substituents [reactions (*7a*) and (*7b*)].

It is well known that the one-electron oxidation of hydroxycyclohexadienyl-type radicals by $Fe(CN)_6^{3-}$ yields the corresponding phenols (*via* a *bona-fide* carbocation) [*cf.*





reactions (10)–(13)]. The subsequent reactions of another carbocation, *i.e.* that formed by the oxidation of the benzyl-type radical [reaction (15)], will be discussed below.

At pH 7 the G value of $\mathrm{Fe(CN)_6}^{3-}$ consumption has been calculated to be 5.8×10^{-7} mol $\mathrm{J^{-1}}$ (for lower dose $\leqslant 1.5$ Gy/pulse). This value agrees with the one determined after γ-irradiation (Table 2).

The products and their G values are compiled in Table 2. As can be seen from this table, there is a reasonable material balance with respect to the ·OH radicals produced, the products formed and $\mathrm{Fe(CN)_6}^{3-}$ consumed. The products consist mainly of 4-chloro-2-hydroxytoluene and 4-chloro-3-hydroxytoluene, but there are also minor amounts of 4-chlorobenzyl alcohol and 4-chlorobenzaldehyde. The latter products must have the benzyl radical as precursor and from their yields it is calculated that *ca.* 5% of the ·OH radicals must have abstracted an H atom from the methyl group.

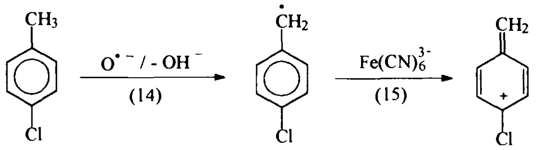
The methyl group in toluene[11,17] (and to a lesser extent the alanyl group in phenylalanine[9]) direct the electrophilic ·OH radical into its *ortho* and *para* positions. In 4-chlorotoluene the *para* position is occupied by the chlorine substituent. Addition at the *para* position would lead to a noticeable absorption by the 4-methylphenoxyl radical at *ca.* 420 nm [$\varepsilon(420) = 1800$ $\mathrm{dm^3\ mol^{-1}\ cm^{-1}}$][18] and a rapid increase in conductivity due to a fast HCl elimination [reactions (7*c*) and (9)]. Pulse-conductometric experiments show that the value of $G(\mathrm{HCl}) \approx 0.2 \times 10^{-7}$ mol $\mathrm{J^{-1}}$ is low, in agreement with the spectral data which show very little absorption at 420 nm (Fig. 1).

Thus, we conclude that the ·OH radicals add with some preference to the 2-position [reaction (7*a*), *ca.* 50%, slightly activated by the methyl group] followed by an addition to the 3-position [reaction (7*b*), *ca.* 40%]. Abstraction from the methyl group [reaction (7*e*), *ca.* 5%] and addition at the *ipso* position of the chlorine substituent [reaction (7*c*), *ca.* 3%] are of minor importance. The ·OH addition at the *ipso* position of the methyl group [reaction (7*d*)] cannot be assessed by this product study, but its contribution must be low (in agreement with other related systems, *cf.* ref. 9).

Products from $\mathrm{O^{\bullet-}}$ reactions; the oxidation of the 4-chlorobenzyl radical by $\mathrm{Fe(CN)_6}^{3-}$

The yields of the products formed under these conditions are compiled in Table 2, column 2. It is seen that the main product is 4-chlorobenzaldehyde with a G value of 3.7×10^{-7} mol $\mathrm{J^{-1}}$. The formation of this product requires three oxidation equivalents. Therefore, together with the other products, an acceptable balance with respect to the consumption of $\mathrm{Fe(CN)_6}^{3-}$ is obtained.

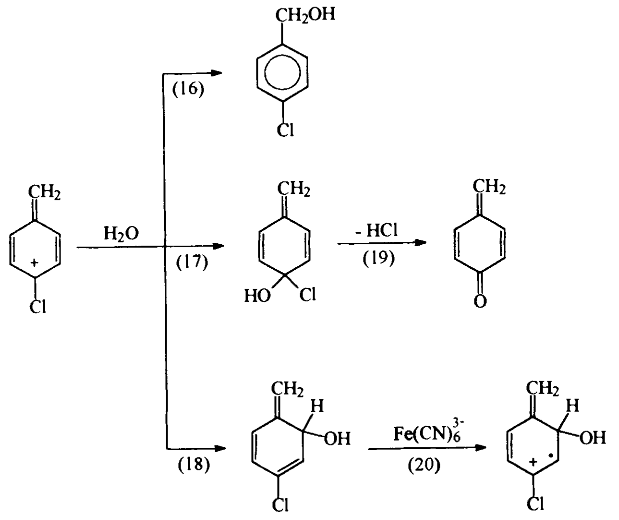
The pK_a value of the ·OH radical is 11.9 ± 0.2.[1] Thus at *ca.* pH = 13.7 (0.5 mol $\mathrm{dm^3}$ NaOH), where the experiments in basic solutions were carried out, the $\mathrm{O^{\bullet-}}$ radicals dominate, but some 1.6–2.5% ·OH radicals are still present in the equilibrium. They react with 4-chlorotoluene slightly faster ($k_7 = 5.5 \times 10^9$ $\mathrm{dm^3\ mol^{-1}\ s^{-1}}$)[19] than the $\mathrm{O^{\bullet-}}$ radicals ($k_8 = 1.4 \times 10^9$ $\mathrm{dm^3\ mol^{-1}\ s^{-1}}$). Assuming that the $\mathrm{O^{\bullet-}}$–·OH equilibrium is fully established during their reactions with 4-chlorotoluene it is calculated that 6–9% of the product yield must be due to ·OH radical reactions. This explains the relatively high yield of the 4-chloro-2-hydroxytoluene and 4-chloro-3-hydroxytoluene formed at pH 13.7 (11.5% of $\mathrm{O^{\bullet-}}$ radicals, Table 2) while firmly indicating that $\mathrm{O^{\bullet-}}$ radicals largely abstract H atoms from the methyl group [reaction (14)] and addition to the ring can be neglected.

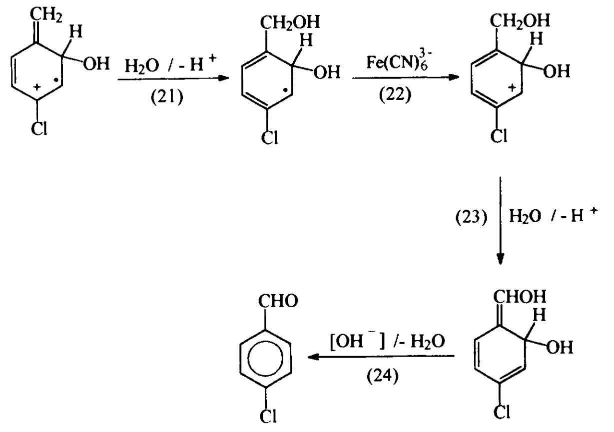


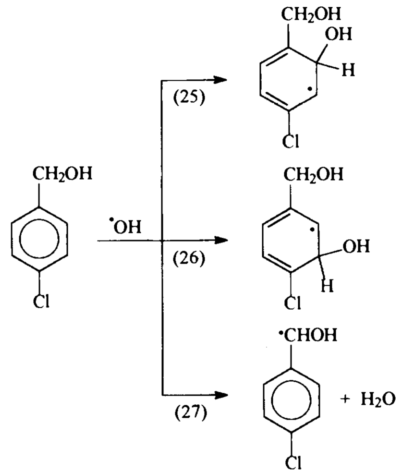
It has been shown above that on the pulse radiolysis timescale $\mathrm{Fe(CN)_6}^{3-}$ is consumed with a G value of *ca.* 6×10^{-7} mol $\mathrm{J^{-1}}$, *i.e.* only one-oxidation equivalent is exchanged. It is suggested that in the fast step the benzyl-type radicals are oxidized to the corresponding carbocation [reaction (15)].

The carbocation will then readily react with water. There are three positions where the OH substituent may be introduced: at the exocyclic methylene position [reaction (16)] or at the 2- and 4-positions of the ring [reactions (17) and (18)].

When the OH-substituent is introduced at the exocyclic methylene group the resulting product is 4-chlorobenzyl alcohol [reaction (16)]. This product is found with a yield of only 8% of the $\mathrm{O^{\bullet-}}$ yield (Table 2). It is reemphasized that 4-chlorobenzyl alcohol is not oxidized to 4-chlorobenzaldehyde by $\mathrm{Fe(CN)_6}^{3-}$ under the conditions of the radiolytic experiments. The product formed in reaction (17) will rapidly lose HCl [reaction (19)]. The resulting quinone methide is unstable at this high pH;[20] the products arising from it have escaped our analysis. This may be one of the reasons why the material balance is poorer at pH 13.7 than at pH 7. The major product, 4-chlorobenzaldehyde cannot be formed *via* reactions







(16) and (17). The water addition in the ring [reaction (18)] is in agreement with the assumption that the chlorine substituent disfavours the accumulation of positive charge at the exocyclic methylene group. The product from reaction (18) is now further oxidized by $Fe(CN)_6^{3-}$ [reaction (20)]. In an attempt to explain the high yield of 4-chlorobenzaldehyde (Table 2) one might suggest that the radical cation formed in reaction (20) could react with water at the exocyclic methylene group [reaction (21)]. The resulting radical could then be further oxidized by $Fe(CN)_6^{3-}$ and react with water [reactions (22) and 23)].

This mechanistic proposal can be tested by studying the reaction of 4-chlorobenzyl alcohol with the ˙OH radical [reactions (25)–(27)] which will produce to a large extent the same radical as that formed in reaction (21) [*cf.* reaction (25)].

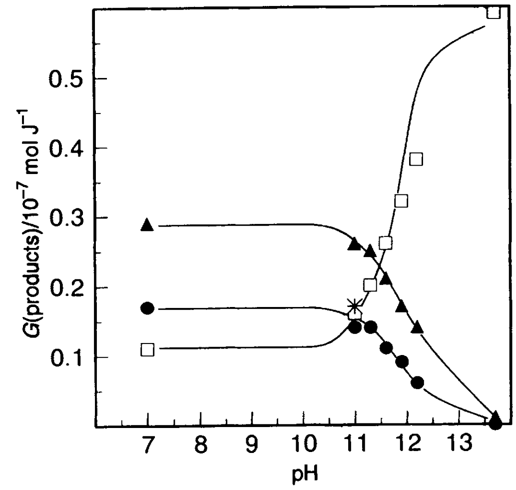
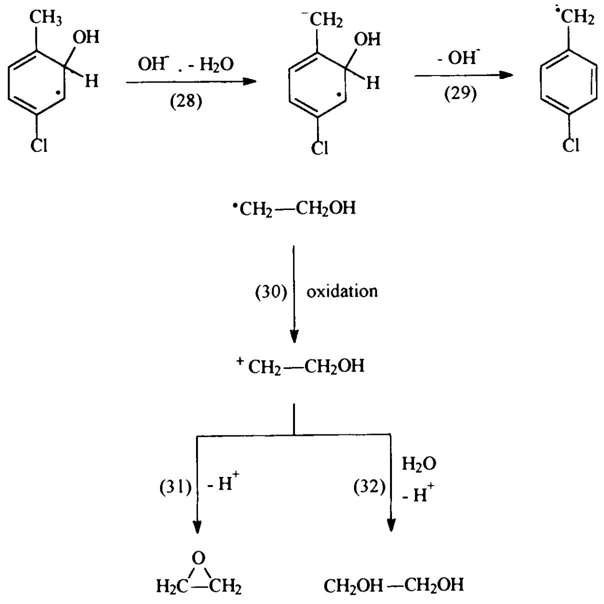


Fig. 4 γ-Radiolysis of an N_2O-saturated aqueous solution of 4-chlorobenzyl alcohol in the presence of $Fe(CN)_6^{3-}$. Yield of 4-chlorobenzaldehyde as a function of pH ([$Fe(CN)_6^{3-}$]: □ 10^{-3} mol dm^{-3}; ✱ 5×10^{-4} mol dm^{-3}). To estimate the yields of 4-chloro-2-hydroxybenzyl alcohol (▲) and 4-chloro-3-hydroxybenzyl alcohol (●) equal absorption coefficients of the phenols and total product yields equal to that of ˙OH–O˙⁻ are assumed.

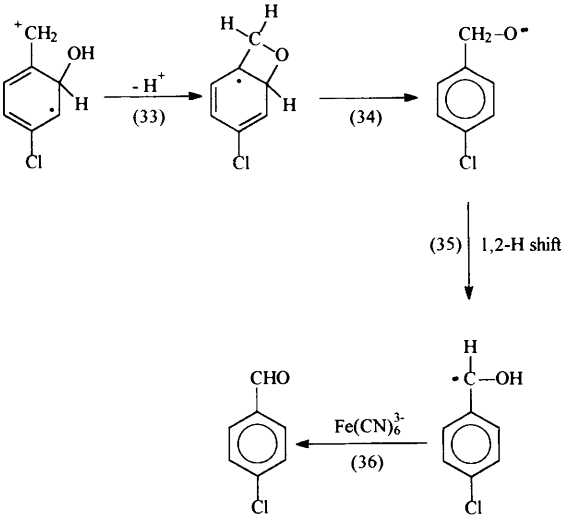


When 4-chlorobenzyl alcohol is γ-irradiated at pH 7 in N_2O-saturated solutions in the presence of $Fe(CN)_6^{3-}$, 4-chlorobenzaldehyde is formed with a *G* value of only 1.1×10^{-7} mol J^{-1}. This low yield can be accounted for by the oxidation of the benzyl-type radicals formed under these conditions [reaction (27)]. This result proves that the oxidation to 4-chlorobenzaldehyde cannot proceed *via* reactions (21)–(24).

Owing to the mode of generation of the benzyl-type radicals in reaction (14) the oxidation reactions have been carried out in strongly basic solutions. Hence it might be possible that the hydroxycyclohexadienyl radical in question undergoes an OH^--induced water elimination [reactions (28) and (29)].

To test this possibility the pH-dependence of 4-chlorobenzaldehyde formation was studied again using 4-chlorobenzyl alcohol as the substrate for reaction of the ˙OH–O⁻ radicals. As can be seen from Fig. 4 the yield of 4-chlorobenzaldehyde increases with increasing pH, but significant yields of this product are only formed in the strongly alkaline pH range where the presence of the O˙⁻ radical trivially [reaction (14)] generates increasing yields of benzyl-type radicals.

Deprotonation at carbon, *e.g.* reaction (28), is usually a slow process and has to compete with the oxidation of the



hydroxycyclohexadienyl-type radical by $Fe(CN)_6^{3-}$. At low OH^- concentrations this water elimination may be too slow to become effective and hence this process could not have been observed. Hence competition experiments have been carried out at pH 11. Although at this pH there is already an increased yield of 4-chlorobenzaldehyde due to the formation of benzyl-type radicals by $O^{\bullet -}$ radicals, the OH^- concentration is already very high which potentially facilitates the water elimination in competition with the oxidation by $Fe(CN)_6^{3-}$. Under these conditions the yield of 4-chlorobenzaldehyde was found to be the same when $Fe(CN)_6^{3-}$ was present either at 10^{-3} or 5×10^{-4} mol dm^{-3}. If under these conditions the water elimination were to take place the 4-chlorobenzaldehyde yield should have been higher at the lower $Fe(CN)_6^{3-}$ concentration. These facts indicate that this mechanistic possibility must also be rejected.

The oxidation of β-hydroxyalkyl radicals by transition metal ions yields epoxides *via* an intermediate carbocation [reactions (30) and (31)].[21] It has been suggested that the intermediate carbocation deprotonates forming the epoxide [reaction (31)] and that a reaction with water yielding the glycol [reaction (32)] must be comparatively slow.

Applying this reaction to the radical cation formed in reaction (20) an intermediate is formed [reaction (33)] which can rearomatize by β-fragmentation [reaction (34)]. The resulting oxyl radical will undergo a rapid 1,2-H shift [reaction (35)] (*cf.* refs. 22–25). The subsequent oxidation of the α-hydroxyalkyl radical by $Fe(CN)_6^{3-}$ [reaction (36)] is a well established reaction.[26]

It is worth mentioning that the 4-chlorobenzyl radical is not unique in the behaviour towards oxidation by $Fe(CN)_6^{3-}$. Oxidation of the unsubstituted benzyl radical [γ-irradiation of 10^{-3} mol dm^{-3} toluene at pH 13.5 in the presence of 10^{-3} mol dm^{-3} $Fe(CN)_6^{3-}$] yielded benzaldehyde with a *G* value of 2×10^{-7} mol J^{-1}. This yield is lower than the corresponding yield of 4-chlorobenzaldehyde from 4-chlorotoluene (Table 2), but with a 30% yield it remains an important product.

It has been noted before that in contrast to $IrCl_6^{2-}$, $Fe(CN)_6^{3-}$ does not undergo ligand transfer in its oxidation reactions.[27] No nitriles are formed in our system confirming this earlier observation. However, if a radical adduct to the ligand were further oxidized, the benzaldehydes could have been formed without the appearance of nitriles. In order to check this potential pathway, methyl radicals were generated from the reaction of dimethyl sulfoxide with $^{\bullet}OH$ radicals[28] in the presence of $Fe(CN)_6^{3-}$. Practically no formaldehyde was formed [$G(CH_2O) = 0.04 \times 10^{-7}$ mol J^{-1}; < 1% of the methyl radical yield]. This rules out any such pathway as an alternative.

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