Studies on Structure–Reactivity in the Reaction of OH Radicals with Substituted Halobenzenes in Aqueous Solutions

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The reaction of OH radicals with a number of substituted halobenzenes ($C_6H_{5-n}X_nY$, where X = F, Cl or Br and Y = CH_3, CH_2Cl, $CHCl_2$, CF_3 or OCH_3) produces a transient absorption band whose λ_{max} is in the range 310–340 nm. This band is assigned to the OH adduct and decayed with second-order kinetics, the bimolecular rate constant being in the region of $0.6 \times 10^9 - 5.0 \times 10^9$ dm^3 mol^{-1} s^{-1}. The OH radical reacts mainly by addition to the benzene ring. The rate constants for the reaction of OH radicals, as determined from formation kinetics studies, are between 1.7 and 9.3×10^9 dm^3 mol^{-1} s^{-1}, and are found to depend on the nature of the substituents. A linear correlation is observed with the Hammett parameter. The distribution pattern for the OH adduct is discussed. The OH adduct can be oxidized by $K_3[Fe(CN)_6]$. The rate constant for the oxidation depends on the position of OH addition and the extent of oxidation on the nature of the substituents. The reaction of O^- with 2-chlorotoluene is by H-atom abstraction (14%), producing an absorption band with λ_{max} = 258 nm, and by addition to the benzene ring (86%), producing absorption bands at 290, 320 and 410 nm. The bimolecular rate constant for the reaction of O^- with 2-chlorotoluene is 2.0×10^9 dm^3 mol^{-1} s^{-1} and $\varepsilon_{320nm} = 2.6 \times 10^3$ dm^3 mol^{-1} cm^{-1}. For the reaction of e_{aq}^- with 2-chlorobenzyl chloride, 44% of the e_{aq}^- react with the Cl of the CH_2Cl group producing an absorption band at 258 nm and 56% react with the Cl of the benzene ring producing an absorption band at 320 nm. The bimolecular rate constant as determined from the decay of e_{aq}^- is 2.2×10^{10} dm^3 mol^{-1} s^{-1}.

The γ-radiation-induced chemical reactions of aqueous solutions of benzene and its substituted derivatives are of current interest.[1,2] The reaction of hydroxyl radicals with arenes are, in general, more widely studied and of particular note, among these, are the reactions with arenes containing electron-donating substituents.[3–14] The meaurement of the rate constants for OH radical addition, the oxidation of OH adducts by various oxidants,[12–14] and the stable products distribution have been the common methods employed in investigating the OH radical addition reaction mechanism.

It is now well known that the OH radical addition is electrophilic in nature and that the *ortho* and *para* isomers of OH adducts of arenes containing electron-donating substituents are more readily oxidized as compared to the *meta* isomers. Further, the rate constants for the oxidation of OH adducts are shown to depend on the nature of the substituents and the redox potentials of the oxidants. For example, Buxton *et al.*[10] have shown that the one-electron oxidation of substituted hydroxycyclohexadienyl radical by a mild oxidant such as $[Fe(CN)_6]^{3-}$ is sensitive to the nature of the substituents whereas the oxidation with a more powerful oxidant, $[IrCl_6]^{2-}$, is mainly diffusion controlled.

We have been interested[15,16] in the reactions of recoil ^{38}Cl atoms with substituted halobenzenes where it is established that these reactions are also electrophilic in nature. Substituted halobenzenes have been chosen for hot-atom chemistry studies as they contain different electron-donating and withdrawing groups and thus form an ideal class of compounds for a study of structure–reactivity relationships. It is therefore felt that an extension of such a study to aromatic hydroxylation of these compounds would be of interest. We report here our results on the reaction of OH radicals with a number of substituted halobenzenes ($C_6H_{5-n}X_nY$, where X = F, Cl or Br and Y = CH_3, CH_2Cl, $CHCl_2$, CF_3 or OCH_3) by pulse and steady-state γ-radiolysis techniques. These studies have been carried out to find the possible site of OH attack, redox properties and the decay mechanism of the OH adduct.

Experimental

Preparation of Solutions.—The solutions were prepared in triply distilled water. The substituted halobenzenes were of high purity (>98%) obtained from Fluka Chemicals and used without any further purification. Other chemicals used were of AR grade. N_2, O_2 and N_2O gases were of Iolar grade and obtained from Indian Oxygen. The reaction of OH radicals was studied in N_2O saturated solutions where e_{aq}^- are quantitatively converted to OH radicals ($K_1 = 9.1 \times 10^9$ dm^3 mol^{-1} s^{-1})[11] with G(OH) = 5.6 (species per 100 eV of absorbed energy) [eqn. (1)].

$$e_{aq}^- + N_2O \longrightarrow OH + OH^- + N_2 \qquad (1)$$

The reaction of O^- was studied in N_2O saturated solutions at pH 13.0 where OH radicals are converted to O^-, eqn. (2).

$$OH + OH^- \longrightarrow O^- + H_2O \qquad (2)$$

The reaction of H atoms was studied in N_2 saturated solutions at pH 0.5 where e_{aq}^- are converted to H atoms and OH radicals

$$e_{aq}^- + H^+ \longrightarrow H + H_2O \qquad (3)$$

are scavenged by *tert*-butyl alcohol, eqns. (3) and (4).

$$(CH_3)_3COH + OH \longrightarrow \dot{C}H_2(CH_3)_2COH + H_2O \qquad (4)$$

The reaction of e_{aq}^- was studied in N_2 saturated solutions containing 0.5 mol dm^{-3} *tert*-butyl alcohol to scavenge OH radicals. The range of concentrations of substituted halobenzene used for the determination of the rate constant was between 10^{-4} and 10^{-3} mol dm^{-3}. For steady-state γ-irradiation experiments, it was maintained at 1.0×10^{-3} mol dm^{-3}.

Irradiations.—Pulse-radiolysis experiments were carried out using high-energy electron pulses (7 MeV, 25 and 50 ns) from a

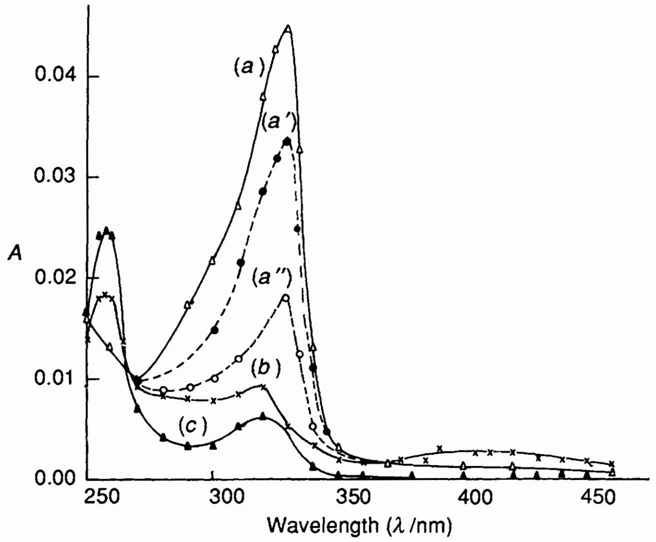


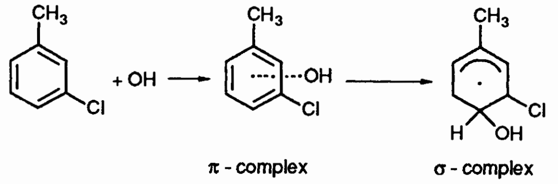
Fig. 1 Transient absorption spectrum on pulse radiolysis of (*a*) an N_2O saturated aqueous solution of 3-chlorotoluene (1.0×10^{-3} mol dm^{-3}, pH 6.0, dose 18.95 Gy per pulse) 0 μs; (*a′*) 20 μs; (*a″*) 100 μs after the pulse; (*b*) an N_2O saturated aqueous solution of 2-chlorotoluene (1.0×10^{-3} mol dm^{-3}, pH 13.0, dose 9.39 Gy per pulse); (*c*) an N_2 saturated aqueous solution of 2-chlorobenzylchloride (1×10^{-3} mol dm^{-3}, pH 6.0, *tert*-butyl alcohol 0.2 mol dm^{-3}, dose 9.39 Gy per pulse).

linear accelerator at BARC. The details of the set-up are published elsewhere.[17] An aerated aqueous solution of KSCN (10 mmol dm^{-3}) was used for monitoring the dose delivered per pulse assuming $G\varepsilon_{500}$ = 21 522 dm^3 mol^{-1} cm^{-1} for 100 eV for the transient $(CNS)_2^-$.[18] Depending upon the pulse width, the dose per pulse was in the range 7–20 Gy. The transient absorption spectrum was obtained at a higher dose while decay analysis was carried out at a lower dose. The transient absorption *vs.* time data were recorded on a storage-scope interfaced to a PC-XT for kinetic analysis.[19] The steady-state γ-irradiations were carried out with a ^{60}Co γ-source having a dose rate of 27 Gy min^{-1}. The total dose absorbed was kept low (80–100 Gy) to prevent any side reactions.

Estimations.—The absorbance of $Fe(CN)_6^{3-}$ was monitored at 420 nm on a Perkin-Elmer spectrophotometer model 3B. $G[-Fe(CN)_6^{3-}]$ values were determined by the linear-regression method from a plot of absorbance *vs.* time for γ-irradiation and using the molar absorption coefficient value of 1000 dm^3 mol^{-1} cm^{-1}. The yield of Cl^- was measured by potentiometric titration using $AgNO_3$ solution.

Results and Discussion

Absorption Spectra of the Transients.—(*a*) *Reaction of* OH *radicals.* Fig. 1(*a*) shows the transient absorption spectrum obtained immediately after pulse radiolysis of an N_2O saturated aqueous solution of 3-chlorotoluene (1.0×10^{-3} mol dm^{-3}, pH 6.0, dose = 18.95 Gy per pulse). This exhibits an absorption band with λ_{max} = 330 nm. It decayed by second-order kinetics with $2k/\varepsilon l = 2.62 \times 10^5$ s^{-1}. In the presence of *tert*-butyl alcohol (0.2 mol dm^{-3}), the reactivity (*Kc*) of OH radicals towards *tert*-butyl alcohol is 1.0×10^8 s^{-1} as compared to a value of 3.5×10^6 s^{-1} towards 3-chlorotoluene and therefore all the OH radicals would be reacting with *tert*-butyl alcohol. The intensity of the 330 nm band reduced considerably (>90%) in the presence of *tert*-butyl alcohol indicating the band to be due to reaction of OH radicals. The small absorption may be due to reaction of H atoms with 3-chlorotoluene as independent studies on reaction of H atoms with 3-chlorotoluene produced a transient absorption band with λ_{max} = 330 nm. The transient absorption spectrum [Fig. 1(*a*)] and its decay kinetics were similar to those observed on pulsing an N_2O saturated aqueous solution of benzene and were assigned to the hydroxycyclohexadienyl radical formed on addition of OH radical to benzene.[20] Therefore, the transient absorption spectrum in the case of 3-chlorotoluene [Fig. 1(*a*)] may also be assigned to OH adduct. A similar argument has also been used for the assignment of the transient band formed on reaction of OH radicals with monofluorobenzene.[21] The first step in the addition of OH radical is the formation of a π-complex, which immediately rearranges to a σ-complex leading to the formation of different isomeric OH adducts. The absorption spectra of the different isomeric forms of OH adducts may be similar.



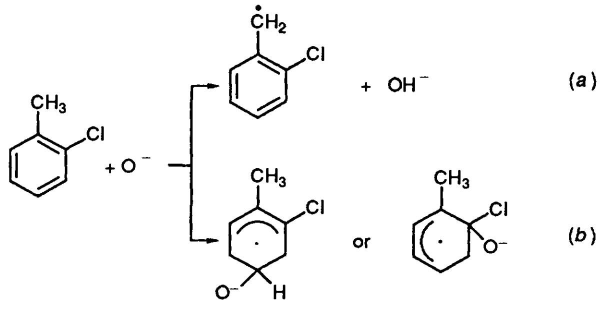
Scheme 1

The OH radical addition reaction was also studied with a number of substituted halobenzenes (Table 1). In all these cases, the nature of the transient absorption spectrum was similar to that for 3-chlorotoluene [Fig. 1(*a*)] but λ_{max} varied between 310 and 340 nm. The molar absorption coefficient, ε, for these transient bands was determined assuming that all the OH radicals react with substituted halobenzene to form the transient species absorbing in the region 310–340 nm. This assumption seems to be valid as the reactivity (*Kc*) of OH towards OH radicals and substituted halobenzenes, under the experimental conditions employed, are *ca.* 6.0×10^4 and 5.0×10^6 s^{-1}, respectively, indicating that all the OH radicals are reacting with substituted halobenzenes. The values of ε thus calculated are also shown in Table 1. From these ε and $2K/\varepsilon l$ values, the bimolecular decay constant for the transient band formed on reaction of OH radicals with substituted halobenzenes is estimated and is shown in Table 1.

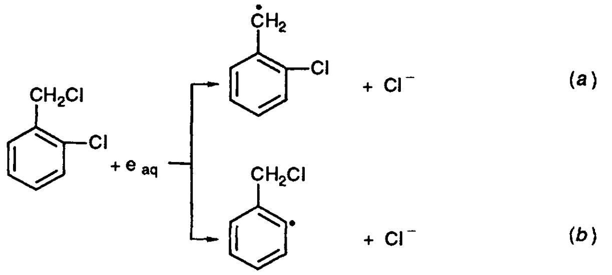
(*b*) *Reaction with* O^-.—A few pulse radiolysis experiments were also carried out at pH 13.0, in order to ascertain the differences in the reactions of OH and O^-. The major reactive species in N_2O saturated solutions at this pH is expected to be O^- as the p*K* for reaction (2) is 11.9.[22] Roughly 10% of OH radicals may be present at this pH. The transient absorption spectra in the case of reactions of O^- with 2- and 3-chlorotoluene and 3,4-dichlorotoluene were similar in nature, but these spectra were different from those obtained on reaction with OH radicals. Fig. 1(*b*) shows the transient absorption spectrum obtained on pulse radiolysis of an N_2O saturated aqueous solution of 2-chlorotoluene (1.0×10^{-3} mol dm^{-3}, pH 13.0, dose 9.39 Gy per pulse). It exhibits absorption bands with λ_{max} = 258 and 320 nm, and broad absorption bands in the region of 290 and 410 nm. Since the transient absorption spectrum [Fig. 1(*b*)] is entirely different from that obtained on reaction with OH radicals [Fig. 1(*a*)], it could not be due to the 10% of OH radicals which may be present at pH 13.0. The reactivity of the OH radicals is not expected to change with pH of the solution to such an extent that an entirely different type of spectrum results. At best, 10% of the absorbance at 320 nm may be due to reaction of OH radicals. O^- could react with 2-chlorotoluene by H-atom abstraction and addition reactions as shown in Scheme 2. The addition of O^- may take place at any carbon position. In order to distinguish between these two pathways, reaction of e_{aq}^- with 2-chlorobenzyl chloride was investigated. If e_{aq}^- reacts with the Cl of the $-CH_2Cl$ group by a dissociative electron-capture process [Scheme 3(*a*)], a transient species similar

Table 1 Physical properties of OH adducts of various substituted halobenzenes

Compound no.	Substituted halobenzenes	λ_{max}/nm	ε_{max}/dm^3 mol^{-1} cm^{-1}	Formation rate constant/10^{-9} dm^3 mol^{-1} s^{-1}	Bimolecular decay/10^{-9} dm^3 mol^{-1} s^{-1}	σ_{calc}	Probable site of OH attack
1	2-Chlorotoluene	325	3600	6.5	5.0	−0.17	2
2	3-Chlorotoluene	330	4200	3.5	1.1	−0.11	4
3	4-Chlorotoluene	310	4000	5.5	4.7	−0.31	4
4	3,4-Dichlorotoluene	325	1400	1.7	0.6	—	—
5	3,4-α-Trichlorotoluene	330	3500	2.5	1.8	+0.34	4
6	2,6,α,α-Tetrachlorotoluene	325	1500	4.9	0.7	—	—
7	2-Chloro-6-fluorotoluene	330	2900	4.2	3.1	+0.40	2
8	3-Chlorofluorobenzene	320	3000	4.8	3.1	—	—
9	3-Chlorobenzotrifluoride	320	2700	2.0	0.7	+0.72	4
10	2-Chlorobenzyl chloride	315	2800	4.1	1.9	+0.10	5
11	3-Chloroanisole	340	5100	9.3	3.7	−0.58	4
12	3-Bromotoluene	330	5300	4.9	2.3	−0.10	4



Scheme 2



Scheme 3

to that shown in Scheme 2(*a*) would be formed. The reaction of e_{aq}^- with 2-chlorobenzyl chloride may also take place with Cl attached to the benzene ring [Scheme 3(*b*)]. The rate constant for the reaction of e_{aq}^- with 2-chlorobenzyl chloride was determined by following the decay of e_{aq}^- at 720 nm for different concentrations of 2-chlorobenzyl chloride. The decay of e_{aq}^- becomes faster and of first order. The bimolecular rate constant as determined from the slope of the linear plot of pseudo-first-order rate *vs.* 2-chlorobenzyl chloride concentration was 1.0×10^{10} dm^3 mol^{-1} s^{-1}. Fig. 1(*c*) shows the transient absorption spectrum obtained on pulse radiolysis of an N_2 saturated aqueous solution of 2-chlorobenzyl chloride (1.0×10^{-3} mol dm^{-3}, *tert*-butyl alcohol concentration 0.2 mol dm^{-3}, pH 6.0, dose 9.39 Gy per pulse). It exhibits absorption bands with $\lambda_{max} = 258$ and 320 nm. The broad absorption bands in the region of 290 and 410 nm were not present in this case. λ_{max} and decay of the transient band (258 nm) matches with that of the benzyl radical formed on reaction of e_{aq}^- with benzyl chloride.[23] Therefore this band could be due to the 2-chlorobenzyl radical formed *via* the reaction shown in Scheme 3(*a*). Assuming that the molar absorption coefficient of the benzyl radical ($\varepsilon_{258nm} = 2.5 \times 10^4$ dm^3 mol^{-1} cm^{-1})[23] does not change owing to the presence of Cl in the benzene ring, the concentration of the transient species producing the band at 258 nm [Fig. 1(*c*)] is determined to be 1.1×10^{-6} mol dm^{-3}. Under the experimental conditions employed in Fig. 1(*c*), the concentration of e_{aq}^- produced on pulse radiolysis is 2.4×10^{-6} mol dm^{-3}, showing that *ca.* 44% of e_{aq}^- react by the process shown in Scheme 3(*a*). The remaining 56% of e_{aq}^- must be reacting by the process shown in Scheme 3(*b*). The λ_{max}, decay and the relative intensity of the other band (320 nm) formed on reaction of e_{aq}^- with 2-chlorobenzyl chloride [Fig. 1(*c*)] do not match with those of the benzyl radical reported in the literature.[23] Therefore, this band could not be entirely due to the 2-chlorobenzyl radical alone. It is possible that the radical formed *via* the reaction of Scheme 3(*b*) may also have an absorption in this region, which may interfere with the absorption bands of the 2-chlorobenzyl radical. Additional evidence for the reaction of e_{aq}^- with 2-chlorobenzyl chloride *via* the reaction in Scheme 3(*a*) also comes from the fact that reaction of e_{aq}^- with 2-chlorotoluene does not produce an absorption band at 258 nm similar to that shown in Fig. 1(*c*). The reaction of e_{aq}^- with 2-chlorotoluene would be *via* the Cl attached to the benzene ring, similar to the reaction shown in Scheme 3(*b*).

This procedure is employed to determine the individual contributions of the processes shown in Scheme 2 to the reaction of O^- with 2-chlorotoluene. λ_{max} and decay of the band (258 nm) match with that of the benzyl radical. Therefore the band at 258 nm in Fig. 1(*b*) may also be assumed to be due to the 2-chlorobenzyl radical formed *via* the process in Scheme 2(*a*). Taking the molar absorption coefficient to be 2.5×10^4 dm^3 mol^{-1} cm^{-1}, the concentration of the transient species is estimated to be 0.7×10^{-6} mol dm^{-3}, whereas the concentration of O^- is 5.4×10^{-6} mol dm^{-3}. This shows that only *ca.* 14% of O^- reacts by Scheme 2(*a*). Therefore, the remaining 86% of O^- must be reacting by Scheme 2(*b*). Since the fraction of O^- reacting with 2-chlorotoluene by Scheme 2(*a*) is very small, the intensity of the 2-chlorobenzyl radical absorption in the region of 320 nm would also be very small. Therefore, the absorption band with $\lambda_{max} = 320$ nm and broad bands at 290 and 410 nm could be due to addition of O^- to 2-chlorotoluene [Scheme 2(*b*)]. Assuming that 86% of O^- (5.4×10^{-6} mol dm^{-3} total concentration) reacts with 2-chlorotoluene by Scheme 2(*b*), the molar absorption coefficient of the band at 320 nm is estimated to be 2.6×10^3 dm^3 mol^{-1} cm^{-1}. The bimolecular rate constant for the reaction of O^- with 2-chlorotoluene as determined from the growth of the 320 nm band was 2.0×10^9 dm^3 mol^{-1} s^{-1}. It may be concluded that 14% of O^- reacts with 2-chlorotoluene by H-atom abstraction producing an absorption band at 258 nm and the remaining 86% by an addition reaction producing absorption bands at 290, 320 and 410 nm. Similarly e_{aq}^- reacts with 2-chlorobenzyl chloride by dissociative electron capture by

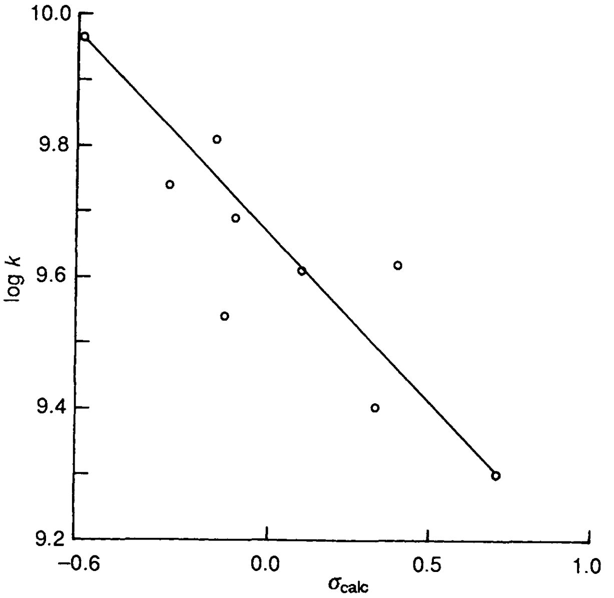


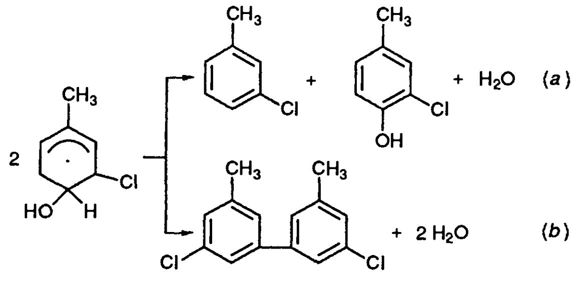
Fig. 2 Log (formation rate constant) *vs.* σ_{calc} for OH radical reaction with substituted halobenzenes

Cl present at both positions. Roughly 44% of e_{aq}^- reacts with the Cl of the CH_2Cl group and 56% with the Cl on the benzene ring.

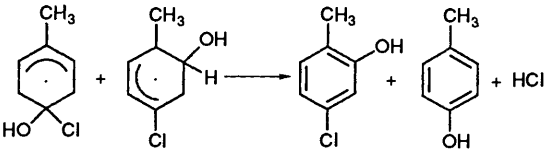
Kinetics for the Reaction of OH *Radicals.*—(*a*) *Kinetics for the formation of* OH *adduct.* The rate constants for the formation of the OH adduct were determined from the build-up kinetics of the transient band for different concentrations of the substrates. The growth of the transient band was first order. The pseudo-first-order rate constant (K_{obs}) was observed to increase linearly with solute concentration. The bimolecular rate constant was determined from the slope of the linear plot of K_{obs} with solute concentration and the values are shown in Table 1. The rate constant for the OH radical addition to substituted benzene was correlated with the Hammett parameter.[3,5,24] It is reported that the *ortho* and *para* positions are more favoured for OH radical addition with benzene derivatives containing electron-donating substituents.[14] In each of the substituted halobenzenes used in the present studies, one of the substituents is a halogen atom and the other an electron-donating ($-OCH_3$, $-CH_3$) or -withdrawing ($-CF_3$, $-CHCl_2$, $-CH_2Cl$) group at different positions. Therefore, in the present studies, the correlation of the rate constant with the Hammett parameter is not straightforward. We have used the algebraic sum of the Hammett constants (σ_p^+ or σ_m^+)[24] for *para* and *meta* substitution and the Taft constant (σ^*)[25] for the *ortho* substitution, to determine the more probable site for OH attack, where the σ value (σ_{calc}) is expected to be a minimum. The minimum σ_{calc} value for different compounds is shown in Table 1. This procedure seems to be valid, since the slope (ρ^+) calculated from the Hammett plot (Fig. 2) is found to be -0.52, which is in fair agreement with the reported values of -0.5 and -0.4 for some of the substituted benzenes.[3,5] The distribution pattern for OH attack can be estimated by assuming that the site with maximum σ value has zero probability for OH attack. This normalization procedure shows that the OH attack is more than 70% at the more likely site (position 4) in the case of 4-chlorotoluene, while it is *ca.* 35% for other compounds indicating that the attack on other positions is also likely but with lower probability. The more probable site for OH attack is also shown in Table 1.

The rate constants for the addition of OH radicals to different substituted halobenzenes are in the range 1.7–9.3 × 10^9 $dm^3\ mol^{-1}\ s^{-1}$, which suggests that it is a diffusion-controlled process and excludes the possibility that the transient band is due to a species formed on H-atom abstraction by OH radicals. These rate constant values represent the lower limit of diffusion-controlled reaction rates and show a linear relationship with Hammett parameter. The diffusion levelling is expected to take place for those substituted halobenzenes having a lower Hammett constant, which could not be studied owing to the lack of available substituted halobenzenes in this region. It is found to depend on the nature of substituents present in the benzene ring, which is due to the different electron densities at different sites. The rate constant values, although a measure of the overall rate of addition, may be taken to represent the rate constant for the more likely site of OH radical addition.

(*b*) *Decay of* OH *adduct.* The absorption spectra of OH adducts in all systems exhibit a decrease in the absorbance with time after pulse radiolysis [Fig. 1(*a*)]. The decay was analysed[19] for both first- and second-order processes but good correlation was obtained only for the second-order processes. This suggests that the decay occurs by disproportionation or dimerization. The bimolecular rate constants are given in Table 1. Taking a typical example of 3-chlorotoluene, the decay scheme may be written as shown in Scheme 4. In the case of 3-chlorotoluene, steady-state γ-irradiations showed the absence of Cl^-, which supports the decay mechanism and site of OH attack shown in Scheme 4. A similar decay mechanism for the OH adduct of 4-chlorotoluene, if OH addition is at position 4 alone, is unlikely. The disproportionation reaction for the OH adduct of 4-chlorotoluene, when OH addition is at positions 4 and 2, may take place as shown in Scheme 5. Similar disproportionation reactions between OH adducts of 4-chlorotoluene, with OH addition at positions 4 and 3 would also give rise to the formation of HCl. The disproportionation of the OH adduct with OH addition at positions 2 and 3 would take place by a mechanism similar to that shown in Scheme 4(*a*). Cl^- is expected to be formed only if the OH addition is at the Cl site. Under steady-state γ-irradiation of 4-chlorotoluene, $G(Cl^-)$ was determined to be 1.0 showing that OH radical addition takes place at the Cl site (position 4), which has also been estimated to be the more probable site of OH attack (Table 1), thus supporting our estimation on the site of OH attack. Formation of Cl^- and F^- from chloro- and fluoro-benzenes has been explained by a similar mechanism.[10] Formation of Cl^- from the OH adduct, with OH addition at Cl, may also take place by the process shown in Scheme 6.[21]



Scheme 4

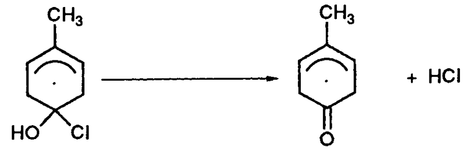


Scheme 5

Table 2 Yields and rate constants for the oxidation of OH adducts of substituted halobenzenes by $Fe(CN)_6^{3-}$

Compound no.	Substituted halobenzenes	$G[-Fe(CN)_6^{3-}]$	σ_{calc}	$K/dm^3\ mol^{-1}\ s^{-1}$ fast	slow
1	Toluene	5.2	−0.31	$1.6 \times 10^{8\,a}$	$1.9 \times 10^{7\,a}$
2	2-Chlorotoluene	3.6	−0.17	—	—
3	3-Chlorotoluene	3.6	−0.11	1.3×10^8	1.3×10^7
4	4-Chlorotoluene	—	−0.31	5.0×10^8	7.0×10^7
5	3,4-Dichlorotoluene	3.5	—	—	—
6	2-Chloro-6-fluorotoluene	3.1	+0.04	—	—
7	3-Chlorobenzotrifluoride	0.9	+0.72	—	—
8	3-Chloroanisole	5.6	−0.58	—	—
9	3-Bromotoluene	4.7	−0.10	—	—

[a] From ref. 10.



Scheme 6

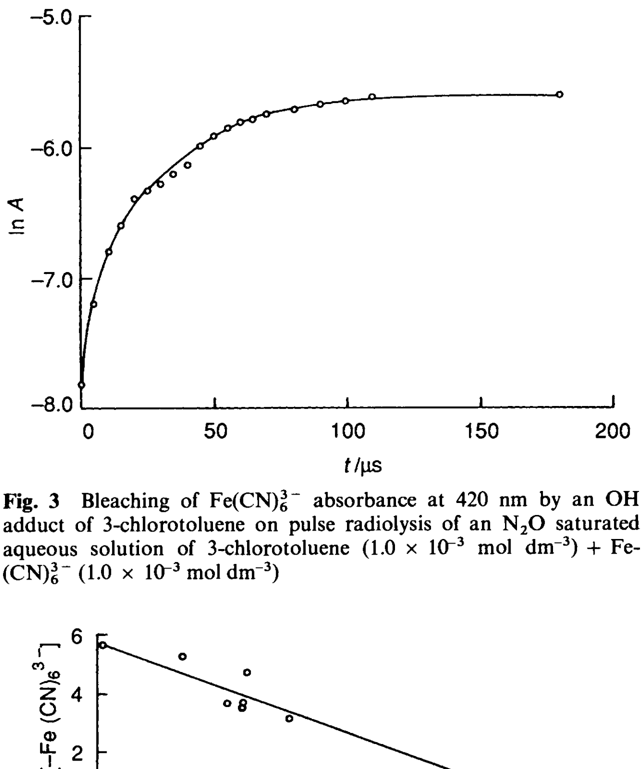


Fig. 3 Bleaching of $Fe(CN)_6^{3-}$ absorbance at 420 nm by an OH adduct of 3-chlorotoluene on pulse radiolysis of an N_2O saturated aqueous solution of 3-chlorotoluene (1.0×10^{-3} mol dm^{-3}) + $Fe(CN)_6^{3-}$ (1.0×10^{-3} mol dm^{-3})

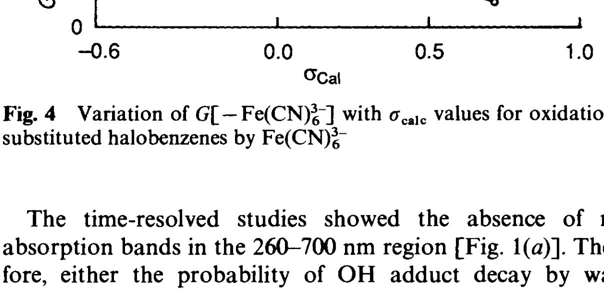


Fig. 4 Variation of $G[-Fe(CN)_6^{3-}]$ with σ_{calc} values for oxidation of substituted halobenzenes by $Fe(CN)_6^{3-}$

The time-resolved studies showed the absence of new absorption bands in the 260–700 nm region [Fig. 1(*a*)]. Therefore, either the probability of OH adduct decay by water elimination is very small or the transient species formed is not absorbing in the 260–700 nm region. However, second-order decay supports the reactions shown in Scheme 4. In the absence of detailed product analysis, it is difficult to determine the contribution of individual processes. The contribution from Scheme 6 may be small because if it had a major contribution, the transient band of the OH adduct would have decayed by a first-order process.

Oxidation of OH *Adduct by* $K_3[Fe(CN)_6]$.—The oxidation of the OH adduct by $Fe(CN)_6^{3-}$ can be monitored either by observing the decay of transient band of the OH adduct or by following the growth of the transient band of the oxidation product. The oxidation of the OH adduct of 3-chlorotoluene could be represented as shown in eqn. (5). $Fe(CN)_6^{3-}$ has a

$$HOC_6H_4ClCH_3 + Fe(CN)_6^{3-} \longrightarrow HOC_6H_4ClCH_3^{+} + Fe(CN)_6^{4-} \quad (5)$$

high absorbance at 320 nm, therefore, the decay of the OH adduct could not be monitored in order to obtain the rate constant for reaction (5). Time-resolved pulse radiolysis studies of an N_2O saturated aqueous solution of 3-chlorotoluene (1.0×10^{-3} mol dm^{-3}) in the presence of $Fe(CN)_6^{3-}$ (1.0×10^{-3} mol dm^{-3}) showed the absence of any new absorption band. Therefore, the rate constant studies could not be carried out from build-up kinetics. However, $Fe(CN)_6^{3-}$ has a weak absorption at 420 nm and the reaction could be studied by monitoring the bleaching of $Fe(CN)_6^{3-}$ at 420 nm. Fig. 3 shows the variation in the absorbance of the $Fe(CN)_6^{3-}$ band at 420 nm on pulse radiolysis of an N_2O saturated aqueous solution of 3-chlorotoluene (1.0×10^{-3} mol dm^{-3}) + $Fe(CN)_6^{3-}$ (1.0×10^{-3} mol dm^{-3}). It is clear from this figure that the oxidation consists of two processes. The rate constant values (K) for fast and slow processes are shown in Table 2. It has been reported [10] that the oxidation of OH adducts of toluene by $Fe(CN)_6^{3-}$ consists of two components, a fast one due to oxidation of the *ortho* and *para* OH adducts and a slower one due to oxidation of the *meta* OH adduct. It is possible that the two different components observed for oxidation of 3- and 4-chlorotoluenes may also be due to different isomers of OH adducts. The rate constants for the oxidation of 4-chlorotoluene by $K_3Fe(CN)_6$ are higher than those of toluene and 3-chlorotoluene. This may be due to the fact that OH addition is mainly at the 4 position where the electron density is high and it also happens to be an *ipso* site.

$G[-Fe(CN)_6^{3-}]$ values determined for the oxidation of OH adducts of various substituted halobenzenes are shown in Table 2. Note the dependence on the nature of substituents present in the benzene ring. Linear correlation is observed on plotting $G[-Fe(CN)_6^{3-}]$ *vs.* σ_{calc} (Fig. 4), indicating that the extent of oxidation depends on the nature of substituents present in the benzene ring.

Comparison of Radiation-induced Hydroxylation and Recoil Halogenation of Substituted Halobenzenes.—The recoil halogenation and radiation-induced hydroxylation of substituted halobenzenes are expected to be similar in nature as both the reacting species are weakly electrophilic. The structure–reactivity correlation was obtained from the rate constant values for hydroxylation with substituted halobenzenes determined from pulse-radiolysis studies. The determination of rate constants in recoil halogen atom studies is not possible. Therefore, the labelled thermal halogen for halogen or labelled thermal halogen for H atom substitution yields are considered to represent the relative reactivities and are related to the Hammett parameter. The ρ^+ values obtained for aromatic chlorination and bromination by recoil methods are -0.56 and -0.45, respectively,[26] which are comparable to the observed value of -0.52 for aromatic hydroxylation of substituted halobenzenes (Fig. 2). It is therefore interesting to compare the relative distribution of OH attack with monochlorotoluenes (*ortho*, *meta* and *para*) as evaluated from the σ^+ values in our present study with the reported[27] *ipso* addition yields observed in recoil reactions of the ^{38}Cl atom with the same compounds. The ratios for *ipso* addition for *ortho*-, *meta*- and *para*-chlorotoluenes are 39:6:55 for recoil chlorination and 32:17:51 for hydroxylation indicating that the processes are similar in nature.

Conclusions

The OH radicals react with substituted halobenzenes by an addition reaction forming a transient absorption band in the region 310–340 nm. The formation rate constant is observed to depend on the nature of the substituents on the halobenzenes. The addition of O^- (86%) to substituted halobenzenes (2-chlorotoluene) produces transient bands at 290, 320 and 410 nm whereas H-atom abstraction by O^- (14%) produced a transient band at 258 nm. $Fe(CN)_6^{3-}$ is able to oxidize the OH adduct. The rate constant for the oxidation is found to depend on the position of OH attack and the extent of oxidation depends on the nature of the substituents present in the benzene ring. e_{aq}^- reacts with 2-chlorobenzyl chloride by dissociative electron capture *via* the chlorine present at either position, 44% react with the Cl of the CH_2Cl group and 56% with the Cl of the benzene ring.

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