Reactions of OH and SO₄⁻⁻ with Some Halobenzenes and Halotoluenes: A Radiation Chemical Study

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The optical absorption and kinetic characteristics of the transients formed in the reactions of OH and SO₄^{•-} with bromobenzene, *ortho* and *meta*-isomers of chloro- and bromobenzenes, and monobromotoluenes have been studied by pulse radiolysis technique. The rates for OH reaction are generally higher ($k = (1.7-4.4) \times 10^9$ M⁻¹ s⁻¹) than those found for the SO₄^{•-} reaction ($k = (0.4-2.3) \times 10^9$ M⁻¹ s⁻¹). ρ^+ values of -0.4 for OH and -1.2 for SO₄^{•-} reactions were obtained from the Hammett analysis. The formation of substituted hydroxycyclohexadienyl radicals ($\lambda_{max} = 315-330$ nm) is the major reaction channel, and the phenoxyl type radical ($\lambda \ge 400$ nm) formation is an additional minor process in the SO₄^{•-} reaction. Abstraction of H by SO₄^{•-} from the -CH₃ group is only significant with the *para*-isomers of bromo- and chlorotoluenes. This result is in accord with the observed yields (70% of SO₄^{•-}) of the products resulting from the oxidation of the 4-chlorobenzyl radical in the presence of K₃Fe(CN)₆ under steady-state conditions. The total yields of the phenolic products accounting for >90% of OH and SO₄^{*-} suggest that the attack at the *ipso* positions is considerably small. The rate constants for OH reactions relative to benzene at positions 3 and 6 of 2-chlorotoluene and positions 2 and 3 of 4-chlorotoluene are between 1.18 and 1.39, indicating that the directing effects of -CH₃ and -Cl groups are comparable. This is also reflected in the additive effects of activation of the *ortho* and *para*-positions and deactivation of *meta*-positions by these substituents in 3-chlorotoluene.

Introduction

The reactions of primary radiolytic products of water (OH, e_{aq}^{-} , and H)

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

and the secondary radicals ($SO_4^{\bullet-}$, $Cl_2^{\bullet-}$, alcohol and peroxyl radicals, etc.) derived from them with benzene and its derivatives have been the subject of recent interest.¹⁻⁷ This stems from the fact that radiation chemical methods are particularly well suited for the investigation of the substituent effects in arenes as the radiation chemical yields of the reactive species are precisely known and low concentrations of solutes can be used.

The OH radical is highly reactive toward arenes $(k > 10^9 \text{ M}^{-1} \text{ s}^{-1})$ and is shown^{3-6,8-12} to react by addition to the aromatic ring to form the hydroxycyclohexadienyl radical which has the characteristic absorption in the range 310–330 nm. These studies—dealing with the effects of the substituent on the rate of the reaction and orientation—were, however, limited mostly to monosubstituted benzene derivatives. Chen and Schuler⁶ have quantified the directing effects of the $-C_6H_5$ group in biphenyl. Such studies are, however, lacking with disubstituted benzenes. The objective of this study is to investigate these effects in such compounds since they would not only allow a quantitative comparison of the competing directing effects of the substituents but also render the possibility of examining the extent of ipso substitution.

Disubstituted benzenes of the type $C_6H_{5-n}X_nY$ (where X = halogen and Y = -Cl, -Br, -CH₃, -CH₂Cl, -CHCl₂, -CF₃, or -OCH₃) seem to form an interesting class of compounds for obtaining information on the structure-reactivity relationship with OH and other oxidizing radicals as the reacting species. Our

recent work^{4,7} on pulse radiolysis has shown differences not only in the reaction pathways between OH and $SO_4^{\bullet-}$ attack but also in the extent of a particular reaction channel in the case of $SO_4^{\bullet-}$ reaction with isomers of chlorotoluenes. Furthermore, these isomers are well suited for estimates of the extent of the ipso attack by OH at the C-Cl position due to the *ortho* and *para* directing nature of the -CH₃ group. Product analysis studies are, therefore, needed to clearly establish the reaction mechanism.

The procedure employed in product studies usually involves the conversion of the intermediate hydroxycyclohexadienyl radicals into stable products on a time scale that is fast compared to the competing decay reactions by using sufficiently reactive and selective reagents. Such studies on some substituted benzenes (e.g. anisole, benzoic acid, biphenyl, fluorobenzene, phenol, toluene, xylenes, etc.) using inorganic oxidants $(Fe(CN)_6^{3-} (E^{\circ}$ = 360 mV) and $IrCl_6^{2-}$ (E° = 870 mV) have already been reported.^{6,11,13-17} HPLC methods, with the recent availability of photodiode array detectors, have become particularly valuable in the determination of the distribution pattern of the stable isomeric products in mixtures of complex molecules. The usefulness of this technique was demonstrated in the recent studies⁶ on the radiolytic oxidation of substituted naphthalenes and biphenyls where micromolar quantities of the products formed in the lowdose range were accurately measured.

The present study also involves product analysis to correlate with pulse radiolysis data reported^{4,7} by us on the reactions of OH and SO₄^{•-} with chlorotoluenes to gain an insight into the directing effects of both the $-CH_3$ and -Cl groups. The results from pulse radiolysis of chloro- and bromobenzenes and chloroand bromotoluenes are also discussed.

Experimental Section

Preparation of Solutions. The halobenzenes and halotoluenes used in this study were obtained from Fluka and were of high purity (>98%). Other chemicals used were of Analar grade. The

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solutions were prepared in water purified by the Millipore Milli-Q system. Experiments were carried out at amibent temperature (22-25 °C).

The reaction of OH radicals was studied in N₂O saturated solutions, containing different solutes (pH = 7), where e_{aq} are quantitatively converted into OH radicals ($k_2 = 9.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$).⁸

$$e_{aq}^- + N_2 O \rightarrow OH + OH^- + N_2$$
 (2)

SO₄⁻⁻ radicals were produced by the reaction of $e_{aq}^{-}(k_3 (e_{aq}) = 1.1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1})$ and H ($k_3(\text{H}) = 2.5 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$) with peroxydisulfate anion¹⁸ in N₂ saturated solutions containing 15 mM K₂S₂O₈, 0.2 M *tert*-butyl alcohol, and varying concentrations (0.1–1.0 mM) of the solute.

$$e_{aq}^{-}(H) + S_2 O_8^{2-} \rightarrow SO_4^{2-}(HSO_4^{-}) + SO_4^{*-}$$
 (3)

Under our experimental conditions, the OH radicals will be scavenged by *tert*-butyl alcohol, while e_{aq} reacts quantitatively with $S_2O_8^{2-}$ (reaction 3). Also a fraction of H (about 30%) is expected to yield $SO_4^{\bullet-}via$ reaction 3 and the estimated¹⁹ $G(SO_4^{\bullet-})$ = 3.3 ($G(e_{aq}^{\bullet})$ at high $S_2O_8^{2-}$ concentration + 0.3G(H)). The contribution (<10%) of H atom reaction with the solute, being negligible, is not taken into consideration in both OH and $SO_4^{\bullet-}$ reactions.

Irradiations. High-energy electron pulses (7 MeV, 50 ns) from a linear accelerator were used for pulse radiolysis experiments, and the details of the facility used have been described elsewhere.²⁰ Dosimetry was carried out with aerated aqueous solutions of 10 mM KSCN solution by optical measurements, taking $G\epsilon_{500} =$ 21 500 M⁻¹ cm⁻¹ per 100 eV for the transient²¹ (SCN)₂^{•-}. The dose per pulse was in the range 1–2 krad. The transient absorption as a function of time was recorded on a storage oscilloscope interfaced to a computer for kinetic analysis.²² For steady-state experiments, a ⁶⁰Co γ -source was employed. The dose rate determined by the Fricke dosimetry was 3.6 krad min⁻¹.

Separation and Estimation of the Reaction Products. The HPLC system from Perkin-Elmer (Series 10 Liquid Chromatograph) coupled to a LC-235 photodiode array detector with GP 100 printer and reverse phase C-18 column (125 mm \times 4.6 mm, 5- μ m packing) was used for the determination of the yields of the products. The column effluent was monitored at 280 nm. The solvent was 60% methanol, and a flow rate of 0.6 mL min⁻¹ was used.

The standards, 5-chloro-2-hydroxytoluene and 2-chloro-5hydroxytoluene, were obtained commercially, whereas others were prepared either by employing the Fenton reaction or by collecting sufficient amounts of irradiation products. These products were characterized from their NMR and UV spectra. The identification of the products formed from irradiation was further confirmed using internal standards. The G-values were determined from the HPLC chromatograms obtained for both the reference compounds and the irradiation products under identical experimental conditions.

Results and Discussion

I. Transient Absorption Spectra. (i) Reaction of OH radical. Optical absorption spectra of the intermediate transients formed in the reaction of OH with chloro- and bromobenzenes and chloroand bromotoluenes were monitored in the range 260–570 nm. The spectra exhibit absorption maxima around 325–330 nm with both ortho- and meta-isomers of dichlorobenzenes, dibromobenzenes, and bromotoluenes (Figure 1). The λ_{max} values and the molar extinction coefficients of the transients, determined assuming a radiation chemical yield of 5.6 for G(OH), are tabulated in Table 1. Also included in this table are the



Figure 1. Transient absorption spectra recorded 2 μ s after the pulse obtained in the reaction of OH with (A) 1,2-dichlorobenzene (×), 1,3-dichlorobenzene without (Δ) and with 0.2 M *tert*-butyl alcohol (O); (B) 2-bromotoluene (\Box), 3-bromotoluene (O), and 4-bromotoluene (\bullet). Dose per pulse = 2 krad; pH = 7; [solute] = 10⁻³ M.

TABLE 1: Values of k (10⁹ M⁻¹ s⁻¹), λ_{max} (nm), and ϵ (M⁻¹ cm⁻¹) Obtained in the Reactions of OH and SO₄⁻⁻ with Some Halobenzenes and Halotoluenes

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compound	ОН	SO4*-	$\lambda_{\text{max}}(\text{OH})$	e	$\lambda_{max}(SO_4^{\bullet-})$
bromobenzene	4.4	1.8			320, 400
chlorobenzene ^{a,b}	5.5	1.5	325	4600	325, 400
1-bromo-2-chlorobenzene	2.0	0.7	330	3800	325, 425
1,2-dibromobenzene	2.3	0.4	330	3200	330, 435
1,3-dibromobenzene ^b	1.9	0.5	330	4800	330
1,2-dichlorobenzene	2.5	0.6	325	3800	320
1,3-dichlorobenzene	2.2	1.1	330	5300	330
2-bromotoluene	1.7	2.3	330	3450	315, 435
3-bromotoluene ^{b,c}	4.9	1.7	330	5200	320
4-bromotoluene	2.9	1.0	315	3700	275, 325
2-chlorotoluene ^{b,c}	6.5	1.7	325	3600	320
3-chlorotoluene ^{b,c}	3.5	0.9	330	4200	325
4-chlorotoluene ^{b,c}	5.5	1.1	310	4000	270, 315

^a Taken from ref 8 for OH reactions. ^b Taken from ref 7 for SO₄^{*-} reactions. ^c Taken from ref 4 for OH reactions.

corresponding values obtained from our recent work^{4,7} on related compounds.

The transients were assigned to the corresponding substituted hydroxycyclohexadienyl radicals based on the ESR²³ and optical absorption⁹ data reported earlier. Furthermore, the band at 330 nm has disappeared (Figure 1) on pulsing N₂O saturated solutions of 1 mM 1,3-dichlorobenzene containing 0.2 M *tert*-butyl alcohol, where the reactivity of OH radical with the solute is lower (k[S]= 1.9 × 10⁶ s⁻¹) by 2 orders of magnitude compared to k[tertbutyl alcohol] 1.5 × 10⁸ s⁻¹ with *tert*-butyl alcohol. In these solutions, almost all of the OH radicals (>98%) are scavenged by *tert*-butyl alcohol, and the existence of a very small band is, possibly, due to the reaction of H atom. Thus, the observed spectra represent the weighted average of the isomeric OH adducts formed from the addition of OH to the benzene ring.

A blue shift was observed in the spectra obtained with *p*-bromotoluene ($\lambda_{max} = 315$ nm) compared to its *ortho*- and

meta-isomers which have maxima at 330 nm (Figure 1). Such a behavior was also noticed in the absorption spectra of OH adducts of o- and m-chlorotoluenes ($\lambda = 325-330 \text{ nm}$)⁴ and oand m-xylenes ($\lambda = 326-328 \text{ nm}$)¹⁵ as compared to their paraisomers ($\lambda_{max} = 310 \text{ nm}$). This is also manifest in the more intense absorption spectra observed in the case of meta-isomers. For example, the extinction coefficient for the OH adducts of m-bromotoluene (5200 M⁻¹ cm⁻¹) is higher than that found for its para-isomer (3700 M⁻¹ cm⁻¹).

The red shift in the UV spectra of *ortho* and *meta*-substituted isomeric OH adducts is due to the stabilization of their excited states. The unpaired spin, especially in the OH adducts of *meta*-isomers, is delocalized on both -Cl and $-CH_3$ substituents, and they are therefore relatively more stable than the *para*-isomers. The stabilization of hydroxycyclohexadienyl radicals by $-CH_3$ and halogen groups is evident from the reported^{4,15} bathochromic shifts in the spectra of OH adducts of chloro- and bromobenzenes (325 nm) and toluene (317 nm) relative to benzene (313 nm). This is further corroborated by the recent work of Chen and Schuler⁶ where a more influencing effect of phenyl substituent leading to a more intense and a strong red shift in the transient absorption spectra was seen in the reaction of OH radical with biphenyl.

(ii) Reaction of $SO_4^{\bullet-}$ Radical. The sulfate radical ion was observed to decay with a half-life of about 5 μ s in the absence of any solute. This was attributed⁷ to the H abstraction from *tert*-butyl alcohol (reaction 4) as neither the bimolecular decay of SO₄^{•-} (reaction 5) nor its reaction with S₂O₈²⁻ (reaction 6) under our experimental conditions can compete with this reaction.

$$(CH_3)_3COH + SO_4^{-} \rightarrow (CH_3)_2C(OH)^{\bullet}CH_2 + HSO_4^{-}$$
 (4)
 $(k_4 = 9.1 \times 10^5 \text{ M}^{-1} \text{ s}^{-1})^{24}$

$$SO_4^{\bullet-} + SO_4^{\bullet-} \rightarrow S_2O_8^{2-} \tag{5}$$

$$(k_{5} = 7.6 \times 10^{6} \text{ M}^{-1} \text{ s}^{-1})^{23}$$

$$S_{2}O_{8}^{2-} + SO_{4}^{*-} \rightarrow S_{2}O_{8}^{*-} + SO_{4}^{2-} \qquad (6)$$

$$(k_6 = 6.6 \times 10^5 \text{ M}^{-1} \text{ s}^{-1})^{25}$$

The transient absorption spectra obtained in the reaction of $SO_4^{\bullet-}$ with bromobenzene, 1,2- and 1,3-dichloro- and 1,2- and 1,3-dibromobenzenes are nearly identical, having maxima at 315–330 nm with additional weak bands ≥ 400 nm (Table 1). The species absorbing at 330 nm are formed immediately from the reaction of $SO_4^{\bullet-}$ (reaction 7) as evident from the time resolved



where X = Br or Cl and Y = Br, Cl, or CH₃

optical spectra recorded with bromobenzene (Figure 2) and from the traces monitored at 330 and 460 nm (inset of Figure 2). As the reaction takes about $2 \mu s$ for completion, the broad absorption ≥ 400 nm in the spectrum recorded immediately after the pulse



Figure 2. (A) Time-resolved transient absorption spectra obtained from the reaction of SO₄^{*-} with bromobenzene (\oplus) immediately, (X) 2 μ s, and (\Box) 10 μ s after the pulse. The inset shows the traces for the build up (330 nm) and the decay of absorbance (460 nm) in the case of bromobenzene at a dose of 1.4 krad per pulse. (B) Transient absorption spectra measured 2 μ s after the pulse from the reaction of SO₄^{*-} with 2-bromotoluene (Δ) and 4-bromotoluene (\star). Dose per pulse = 2.0 krad; pH = 5.5; [solute] = 10⁻³ M.

is due to the contribution of $SO_4^{\bullet-}$. No spectral changes are noticed between 2 and 10 μ s except the decay of the intermediate species.

The transient absorption spectra with o- and p-bromotoluenes (Figure 2) show maxima at 315-330 and ≥ 400 nm, whereas only a single peak was observed⁷ at 330 nm with m-bromotoluene. An additional intense peak at 275 nm was observed with the paraisomer as compared to a very weak band in the ortho-isomer. Since these spectral features are similar to those observed with chlorotoluenes, the product analysis study is carried out only with the latter compounds. The proposed⁷ reaction mechanism is briefly depicted in reaction 7.

The OH adduct radical obtained from the SO_4^{*-} reaction is formed by the hydrolysis of the radical cation produced by direct electron transfer (reaction 7a) and/or by the addition/elimination reactions (reactions 7b,c), though the latter seems to be more likely from the observed ρ^+ value of -1.2 (vide infra). The S_N2 type hydrolysis (reaction 7e), being base catalyzed, is unlikely as the pH of our solutions is 5.5. The OH adducts in the presence of Fe(CN)₆³⁻) are oxidized to the corresponding phenolic products (reaction 7g).

The absorption bands \geq 400 nm are attributed to the formation of phenoxyl radicals following the rearrangement of the sulfate radical adducts by the elimination of HSO₃⁻ (reaction 7f) as they are known^{3,16} to absorb \geq 400 nm. The extent of phenoxyl radical formation in halobenzenes is estimated to be about 12–15% of SO₄⁻⁻ based on the extinction coefficient calculated for the hydroxycyclohexadienyl radical formed in the OH reaction.



Figure 3. Hammett plot for the reaction of SO₄^{•-} with substituted benzenes: (1) toluene, (2) 2-bromotoluene, (3) 2-chlorotoluene, (4) 3-chlorotoluene, (5) 3-bromotoluene, (6 and 7) chlorobenzene and bromobenzene, (8) 1-bromo-2-chlorobenzene, (9) 1,2-dichlorobenzene, and (10) 1,3-dibromobenzene. The inset shows the plot of k_{obs} as a function of [bromobenzene]. Dose per pulse = 1.4 krad; pH = 5.5.

The very intense peak at 275 nm obtained in the case of 4-bromotoluene and 4-chlorotoluene⁷ is assigned to the formation of a benzyl type radical by H abstraction from the $-CH_3$ group (reaction 8). This was confirmed by performing an experiment



with N₂O saturated solutions of 4-bromotoluene at pH = 13, where O⁻⁻ is the reactive species (OH \rightleftharpoons H⁺ + O⁻⁻, pK = 11.9).²⁶ The transient absorption spectrum obtained in this case is similar to that obtained in the SO₄⁻⁻ reaction.

II. Evaluation of Rate Constants. The bimolecular rate constants were measured by monitoring the build up at the λ_{max} (315-330 nm) of the transient species and the decay at 460 nm for the reactions of OH and SO4^{•-} radicals, respectively, in the solute concentration range of 0.1-1 mM. The rate constants were determined from the plots of observed first-order rate constant (k_{obs}) versus the solute concentration (Table 1). A very good least squares fit for these plots (inset of Figure 3) was obtained, and the measured rate constants are accurate to within $\pm 15\%$. Because SO₄ - reacts with *tert*-butyl alcohol in the absence of the solute $(t_{1/2} = 5 \ \mu s)$, a value of $1.7 \times 10^5 \ s^{-1}$ for k_{obs} was taken as the Y-intercept (e.g. the inset of Figure 3 for bromobenzene). While the rate constants for the OH reaction represent the lower limit of the diffusion-controlled process $(1.7 \times 10^9 \text{ for})$ 2-bromotoluene to 4.4×10^9 M⁻¹ s⁻¹ for bromobenzene), lower rates, except in the case of 2-bromotoluene, were observed in the SO₄^{•−} reaction (Table 1).

The rate constants for the reactions of both OH and SO_4^{-} are correlated with the Hammett constants using the procedure employed by us earlier,^{4,7} where the minimum σ_{cal} is taken to represent the more probable site of attack. The ρ^+ values obtained are -0.4 and -1.2 for OH and SO₄⁻⁻ reactions, respectively (Figure 3). However, the linear fit of the data in the former case is less satisfactory and is, therefore, not shown in the figure.

The ρ^+ value -0.4 obtained in this work for OH is in agreement with the earlier reported^{4,8} values ($\rho^+ = -0.52$ to -0.4) for some derivatives of benzene. However, the value of -1.2 for the SO₄^{*-} reaction is less negative than that obtained earlier²⁷ ($\rho^+ = -2.4$) for monosubstituted benzenes, but it is closer to that reported⁷ by us for similar disubstituted compounds ($\rho^+ = -1.6$). The less negative value for disubstituted compounds indicates that the outer sphere electron transfer (reaction 7a) suggested²⁷ for monosubstituted benzenes based on a ρ^+ value of -2.4 is less



Figure 4. Chromatograms obtained at 280 nm for OH (a-c) and for SO_4^{-} (d-f) reactions with 2-, 3-, and 4-chlorotoluenes, respectively (dose = 7 krad), and (g) with higher dose (60 krad) for the reaction of OH with 4-chlorotoluene in the presence of 1 mM Fe(CN)₆³⁻. The peak number 5, in chromatograms c and g, corresponds to the solute and ferricyanide in the case of the OH reaction with 4-chlorotoluene. See Table 2 for the identified products.

likely and the addition/elimination process (reactions 7b,c) is more probable.

The positions 2, 4, and 4 with minimum σ_{cal} values of -0.17, -0.11, and -0.31 are the more probable sites for the attack with 2-, 3-, and 4-chlorotoluenes, respectively. This suggests that the attack of OH and SO4 - at -Cl containing positions of ortho- and para-isomers is considerable. But both the para-isomers of bromoand chlorotoluenes have shown deviation from the linear fit in the Hammett plot. The -Cl substituted positions are deactivated due to its electron withdrawing nature, and the reacting species, being electrophilic, seek other unsubstituted electron rich centers. The additional pathway, i.e. H abstraction from the -CH₃ group, was found to be significant only in 4-chlorotoluene. This process may be sterically hindered by the adjacent -Cl substituent in 2-chlorotoluene. This behavior is also reflected in the observed product distribution under γ -radiolysis, where the formation of the products resulting from the oxidation of the ipso-complexes was not seen.

Product Analysis

OH Reaction. The HPLC chromatograms of the products formed in γ -radiolysis of N₂O saturated solutions of 2-, 3-, and 4-chlorotoluenes (1 mM) in the presence of Fe(CN)₆³⁻ (1 mM) are depicted in Figure 4, where the dose delivered was 7 krad. In these solutions, the conversion of e_{aq}^- into OH radicals is quantitative as its reactivity with Fe(CN)₆³⁻ is less by 2 orders of magnitude than with that of N₂O.

The isomers of the phenolic products were almost exclusively formed in the radiation chemical reaction of OH with chlorotoluenes (peak numbers 2-5, 2-4, and 2 and 4 in the chromatograms for 2-, 3-, and 4-chlorotoluenes, respectively) and the same type of products were also obtained from the Fenton reaction when equimolar mixtures of reagents up to 6 mM were used. In 2-chlorotoluene, it was not possible to separate the phenolic products formed from the attack of OH at positions 4 and 5 (peak



Figure 5. Yield versus dose plot for the products formed in the γ -radiolysis of N₂O saturated solution of 3-chlorotoluene (1 mM) in the presence of ferricyanide (1 mM): (\star) 3-chloro-4-hydroxytoluene, (\square) 3-chloro-2-hydroxytoluene, and (Δ) 5-chloro-2-hydroxytoluene. The G-values are calculated from the initial linear portion.

TABLE 2: Absorption Maxima (nm) from the UV Spectra of Separated Products and Their G-Values (Molecules per 100 eV) Obtained in the Reactions of OH and SO₄⁻⁻ with Monochlorotoluenes

compds obtained from comp a	λ _{max} (nm)	G-value OH SO4*-		peak nos. in the chromato- gram (a-f)
a = 2-chlorotoluene				
(1) 2-chloro- α -hydroxytoluene	255	<0.1		1
(2) 2-chloro-3-hydroxytoluene	276	1.1	0.2	2
(3) 2-Chloro-4-hydroxytoluene and	218, 283	2.4	2.8	3
2-chloro-5-hydroxytoluene				4
(4) 2-chloro-6-hydroxytoluene	276	1.3	0.1	5
a = 3-chlorotoluene				
(1) 3-chloro- α -hydroxytoluene	265	<0.1		1
(2) 3-chloro-4-hydroxytoluene	283	2.1	1.4	2
(3) 3-chloro-2-hydroxytoluene	276	0.9	0.2	3
(4) 5-chloro-2-hydroxytoluene	283	2.3	1.6	4
a = 4-chlorotoluene				
(1) 4-chloro- α -hydroxytoluene	265	0.1	0.3	1
(2) 4-chloro-3-hydroxytoluene	279	2.5	<0.1	2
(3) 4-chlorobenzaldehyde	259	0.3	2.0	3
(4) 4-chloro-2-hydroxytoluene	279	2.2	0.9	4

numbers 3 and 4 in Figure 4a). Therefore, their combined yield was estimated assuming that the extinction coefficients of the two isomers (2-chloro-4-hydroxytoluene and 2-chloro-5-hydroxytoluene) are comparable. Similarly, a slight contribution of 4-chlorobenzaldehyde was noticed in the peak obtained for 4-chloro-3-hydroxytoluene (peak number 3 in Figure 4c) monitored at 280 nm with 4-chlorotoluene in the low-dose range. But, at higher doses, two distinct peaks for these products were observed (Figure 4g). The yield of 4-chlorobenzaldehyde in the former case was, therefore, estimated from the chromatograms obtained at 260 nm, where the absorption due to 4-chloro-3-hydroxytoluene was negligible.

The measured absorption maxima values from the UV spectra of the separated products and their G-values are tabulated in Table 2. The G-values were determined from the yield-dose plots which were found to be linear up to 10 krad, as is examplified in Figure 5 for the phenolic products formed in the case of 3-chlorotoluene.

The competing processes for the oxidation process of the OH adducts by $K_3Fe(CN)_6$ are the reactions of OH with $Fe(CN)_6^4$ and with the primary products formed during radiolysis and the bimolecular decay of the intermediate OH adducts. The loss of

OH due to its reaction with the primary products is insignificant, as is evident from the linearity in the yield-dose plots in the low-dose range. However, secondary products were formed at high doses, as can be seen from the chromatogram (Figure 4) obtained for a sample of 4-chlorotoluene irradiated to a dose of 60 krad. The additional peaks which were eluted before the phenolic products (Figure 4g) were attributed to the substituted dihydroxy compounds based on the retention time found for catechol.

Our work⁴ on pulse radiolysis of 3-chlorotoluene has shown that the oxidation of its OH adducts by $Fe(CN)_6^{3-}$ consists of a fast component and slower components, the respective rate constant values being 1.3×10^8 and 1.3×10^7 M⁻¹ s⁻¹ and the corresponding values obtained with 4-chlorotoluene were lower by a factor of 3. As can be seen from Table 2, the G-values for the total phenolic products are 4.8, 5.3, and 4.7 with 2-, 3-, and 4-chlorotoluenes, respectively. The oxidation of OH adducts is almost quantitative (95% of OH) in 3-chlorotoluene, whereas a slightly higher loss, almost 12–15% of OH, was observed with *ortho*- and *para*-isomers, respectively.

Under steady-state conditions employed in our study, the bimolecular decay reactions cannot compete with the oxidation of OH adducts formed from the attack of OH at the unsubstituted positions, as the radical concentrations produced during radiolysis are low and the rate constants for the oxidation of these adducts are comparatively high. However, the bimolecular decay of the ipso-Cl adduct can be an effective process. The oxidation and the disproportionation of these adducts have difficulty in proceeding, since neither the -Cl nor the -OH can attain positive charge and leave the ring. For example, the reaction pathway for the bimolecular decay of the ipso-Cl adduct in 4-chlorotoluene is shown in reaction 9.



A value of 1 for $G(Cl^{-})$ was earlier reported⁴ by us in 4-chlorotoluene in the absence of the oxidant, whereas its formation was not noticed in the case of the *meta*-isomer. The yield of the ipso-Cl complex (17% OH) in the former system is in fair agreement with the loss of OH observed in this study.

Reaction of SO₄^{•-}. Similar to that of the OH reaction, the formation of only phenolic products was observed in the reaction of SO₄^{•-} with 2- and 3-chlorotoluenes. In contrast, the products formed from the OH and SO₄^{•-} reactions with 4-chlorotoluene are different. In the latter case, 4-chlorobenzaldehyde and 4-chloro- α -hydroxytoluene (reaction 8) were the major products and were formed at the expense of chlorocresols. These products must result from the oxidation of benzyl type radical intermediates. Furthermore, the order found for the yields of products arising from the oxidation of benzyl type radical with *mono*chlorotoluenes (*para* > *ortho* ≈ *meta*) is the same as that found⁷ for the intensities of the transient species absorbing at 275 nm.

The G-values for the total products formed from the three isomers account for the almost complete oxidation of the intermediates formed from $SO_4^{\bullet-}$ attack. Further, the observed product distribution suggests that $SO_4^{\bullet-}$ is more selective than that of OH which is consistent with the more negative ρ^+ value (-1.2) formed in the former reaction. The higher selectivity is also evident from the lower $SO_4^{\bullet-}$ reaction rates (Table 1). This selectivity is particularly evident in 2-chlorotoluene, where the



Figure 6. (A) Partial $(10^9 \text{ M}^{-1} \text{ s}^{-1})$ and (B) relative rate constants for the reaction of OH with 2-, 3-, and 4-chlorotoluenes. Values in B are given relative to benzene. k(benzene+OH) being $7.8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, the partial rate constant for reaction of OH with benzene is taken at $1.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. The values for toluene are calculated from the yields reported in ref 16, and those for phenol and biphenyl are taken from ref 6. The correction factor (k(benzene+OH)/(k(solute+OH))) was applied to the observed values to account for the number of reactive sites and overall reaction rates.

yields from the attack of $SO_4^{\bullet-}$ at positions 4 and 5 account for 85% of $SO_4^{\bullet-}$ compared to 43% with the OH radical.

The observed yields, thus, suggest that the attack on the C–Cl position in 2- and 4-chlorotoluenes is either insignificant (SO₄^{•-} reaction) or a minor process (OH reaction) notwithstanding the *ortho* and *para* directing nature of the CH₃ group.

Substituent Effects in OH Reaction

The partial rate constants for the attack of OH at different positions of isomers of monochlorotoluenes were estimated from the observed yields, and the reported⁴ rate constants are tabulated in Table 1. They are, for example, 0.56×10^9 , 1.31×10^9 , and 1.44×10^9 M⁻¹ s⁻¹, respectively, giving a relative ratio of 0.39: 0.91:1, at the 2-, 4-, and 6-positions of 3-chlorotoluene, and the values for the other two isomers are given in Figure 6A. In order to interpret the substituent effects, the data are compared relative to that of benzene taking $k = 7.8 \times 10^9$ M⁻¹ s⁻¹ for the reaction of OH with benzene.⁸ In the case of 2- and 4-chlorotoluenes, the relative rate constants were, however, estimated only at those positions where the product identification is clearly established. The observed relative rate constants are corrected by the factor (k(benzene + OH))/(k(solute + OH)), and these values are shown in Figure 6B.

The relative rate constants for the reaction of OH with toluene $(k = 3 \times 10^9 \text{ M}^{-1} \text{ s}^{01})$, biphenyl $(k = 10.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1})$, and phenol $(k = 10.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1})^6$ are also shown for comparison. The values in toluene, estimated from the reported ¹⁶ G-values of 1.15, 0.55, and 0.6 for o-, m-, and p-cresols respectively, are found to be 1.28, 0.61, and 1.34. In the other two systems, they are taken from the work of Chen and Schuler.⁶

The relative rate constant values of 1.18 and 1.39 at positions 3 and 6 of 2-chlorotoluene indicate that the effects of activation of the *ortho*-positions and the deactivation of the *meta*-positions by $-CH_3$ and -Cl groups are nearly same. A similar trend was also observed in 4-chlorotoluene where the relative rate constants at positions 2 (*ortho* to $-CH_3$ and *meta* to -Cl) and 3 (*ortho* to -Cl and *meta* to $-CH_3$) are comparable. Further, the deactivating effect of the *meta*-position by the methyl and phenyl groups in toluene and biphenyl (the respective relative rate constant values being 0.61 and 0.63) is compensated by the *ortho* directing -Cl group, as is apparent from the value of 1.18 at position 3 of 2-chlorotoluene.

The relative rate constant values of 2.25 and 2.47 at positions 4 and 6 of 3-chlorotoluene which are either *ortho* or *para* to the $-CH_3$ and -Cl groups reveal that both positions are activated to the same extent. A comparison of these values with those observed at the *ortho* (1.28) and *para* (1.34) positions of toluene show the cumulative effect of activation by $-CH_3$ and -Cl groups. Further, this total activation is nearly equal to the *para* directing effect

of the highly electron donating OH group in phenol, having a relative rate constant of 2.12. Similarly, the deactivation of both $-CH_3$ and -Cl groups for the *meta* attack is evident from the complete inactivation of position 5 of 3-chlorotoluene. On the other hand, position 2, though *ortho* to both substituents, has a value close to that of benzene, and this may be due to the steric hindrance. The similarity in the magnitude of the activating effects of the $-CH_3$ and -Cl groups is in line with the expected behavior of the free radical aromatic substitution where all substituents enhance reactivity at *ortho* and *para* positions over that of benzene. This is due to the fact that the character of the OH radical, though slightly electrophilic, is predominantly neutral in nature.

Conclusion

Reaction of OH radicals with chloro- and bromobenzenes, and with bromotoluenes, yields the corresponding OH adducts with the absorption maxima at 315–330 nm. Additional peaks of lower intensity, due to phenoxyl type radicals ($\lambda \ge 400$ nm), were also observed in the SO₄-- reaction. Abstraction of H from the -CH₃ group by SO₄-- was found to be significant when position 4 is substituted by the halogen group. This observation was also substantiated by the product distribution obtained under steadystate conditions.

The expected activation of ortho- and para-positions and the deactivation of the meta-position by $-CH_3$ and -Cl groups are evident from the relative rate constant values estimated from the observed product yields. The results on aromatic hydroxylation of chlorotoluenes reported in this study clearly establish the usefulness of the pulse radiolysis technique along with product analysis by HPLC in providing quantitative information on the directing effects of the $-CH_3$ and -Cl groups.

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