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# Hydroxylation of Chlorotoluenes and Cresols: A Pulse Radiolysis, Laser Flash Photolysis, and Product Analysis Study

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The reactions of $^\bullet$OH, $O^{\bullet -}$ and $SO_4^{\bullet -}$ with 2-, 3-, and 4-cresols were studied by pulse radiolysis, laser flash photolysis, and product analysis techniques. The rates of OH reaction with cresols are very high ($k \approx 1 \times 10^{10}$ M$^{-1}$ s$^{-1}$), whereas $O^{\bullet -}$ was found to be less reactive ($k \approx 2.4 \times 10^9$ M$^{-1}$ s$^{-1}$). The second-order rate constants for $SO_4^{\bullet -}$ reaction with cresols are in the range (3−6) × $10^9$ M$^{-1}$ s$^{-1}$. The transient absorption spectra measured in OH reaction exhibited peaks in the range 295−325 nm with a red shift for the meta isomer. The absorption spectra obtained for $O^{\bullet -}$ reaction with 2-cresol has a peak at 360 nm, which is different from those measured with the *m* and *p* isomers ($\lambda_{\max} = 310$ and 380 nm). The absorption spectra of the transient species in $SO_4^{\bullet -}$ reaction obtained by pulse radiolysis and flash photolysis techniques are similar, with absorption maxima centered around 290 and 390 nm in all three isomers. The intermediates formed in $^\bullet$OH, $O^{\bullet -}$, and $SO_4^{\bullet -}$ reactions are assigned to OH adducts, substituted benzyl radicals, and radical cations, respectively. The rates for oxygen addition to OH adducts of 2-, 3-, and 4-chlorotoluenes and cresols are high, with $k_f$ values lying in the range (1−2.7) × $10^8$ M$^{-1}$ s$^{-1}$. The relatively higher stability constants of peroxyl radicals formed with cresols ($K = k_f/k_r = (2-5) \times 10^4$ M$^{-1}$) than with chlorotoluenes suggest that the product-forming reaction competes effectively with the reverse reaction in cresols. Dihydroxytoluenes with OH groups ortho to each other were only formed in oxygenated solutions of cresols, and the mechanism involves the addition of oxygen to 1,3-type OH adducts at the carbon carrying the hydroxyl function.

## 1. Introduction

Peroxyl radical chemistry of organic and biologically important molecules in aqueous solution has been the subject of current interest (see ref 1 for recent reviews) because of the importance of its role in a variety of processes (e.g. processes occurring in living systems and in the environment). An important aspect that has been well addressed in the recent past is the radiation-induced oxidative degradation of benzenes[2−6] in aqueous solution. The advanced oxidation processes (e.g. $O_3$−$H_2O_2$, $H_2O_2$−UV, electron beam) make use of the high reactivity[7] of the OH radical in the degradation of water pollutants. Radiation chemical methods have proved very useful in the generation of peroxyl radicals because they are superior to other methods (Fenton reaction or photolysis). For example, the product analysis in the Fenton's reaction, even if it proceeds by the OH radical, is complicated due to competing reactions with $Fe^{2+}$, $Fe^{3+}$, and $H_2O_2$. Similarly, high concentrations of $H_2O_2$ are required in the photolytic method, rendering the evaluation of the kinetics more difficult.

In contrast, the yields of the primary radiolytic products of water have been precisely determined, and solute concentrations of ≤$10^{-3}$ M—the normal solubility limit of many organic compounds in water—can be employed. The following sequence (reactions 1−4) depicts the radiation chemical generation of organic peroxyl radicals.

$$H_2O \rightsquigarrow {}^\bullet OH,\ e_{aq}^-,\ H,\ H_2O_2,\ H_2 \tag{1}$$

$$e_{aq}^- + N_2O \rightarrow {}^\bullet OH + N_2 + OH^- \tag{2}$$

$$RH + {}^\bullet OH \rightarrow R^\bullet + H_2O \tag{3}$$

$$R^\bullet + O_2 \rightarrow RO_2^\bullet \tag{4}$$

Our work on peroxyl radical chemistry of the model system chlorobenzene has recently been published.[8] Further, we have also been interested in the recent past in radiation chemical studies[9,10] of OH reaction with substituted benzenes of the type $C_6H_{5-n}X_nY$, where X = halogen, and Y = −Cl, −Br, $-CH_3$ $-CH_2Cl$, $-CHCl_2$, $-CF_3$, or $-OCH_3$. These formed an interesting class of compounds to obtain information on structure-reactivity relationships as they contain electron-withdrawing as well as electron-donating substituents. The use of both pulse radiolysis and product analysis techniques has been necessary in quantifying the activation effects of the $-CH_3$ and −Cl substituents in chlorotoluenes. The determination of the yields of the radiation products by HPLC is rendered easier if all or most of the standard compounds are commercially available. Studies with several monosubstituted benzenes have, thus, been reported.[11] However, the choice is limited in the case of disubstituted benzenes due to lack of the availability of

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standards, and two examples that fulfill this requirement are isomers of monochlorotoluenes and cresols.

In our previous study, we have reported[10] the directing effects of both $-CH_3$ and $-Cl$ groups for $-OH$ attack with monochlorotoluenes in deoxygenated solutions. We now extend our work to oxygenated solutions of monochlorotoluenes and cresols with a view to compare the directing effects of substituents for oxygen addition. Further, reactions of ${}^{\bullet}OH$, $O^{\bullet-}$, and $SO_4^{\bullet-}$ with cresols in deoxygenated solutions were also investigated, as the published work[12,13] on these compounds has been limited. Roder et al.[14] have presented their data on kinetics for OH addition to cresols in acidic and basic media at the recent 20th Miller Conference on Radiation Chemistry. Studies on reaction of $SO_4^{\bullet-}$ with substituted benzenes[10b] and nucleobases[15] using pulse and steady-state radiolysis techniques have been helpful in the elucidation of the ${}^{\bullet}OH$ reaction mechanism. $SO_4^{\bullet-}$ is a one-electron oxidant reactive species ($E° = 2.5$ V) commonly employed by radiation chemists to mimic the direct effect of radiolysis in dilute aqueous solution. There have been several reports[16,17] on photochemical generation of $SO_4^{\bullet-}$ and the determination of its self-reaction rates. However, the earlier work in aqueous solutions with this method is limited to its reactions with cyclic esters[16b] and purines.[17] Also included, therefore, is the study of $SO_4^{\bullet-}$ reaction with cresols by laser flash photolysis.

## 2. Experimental Section

**(A) Preparation of Solutions.** All chemicals used in the present study were of high purity (≥98%) and were commercially obtained either from Fluka or Sisco (India). Cresols were freshly distilled prior to their use. High-purity $N_2$, $N_2O$, and $N_2O/O_2$ (4:1 v/v) gases of Indian Oxygen Ltd. were used for saturation. The solutions were prepared in Millipore-MilliQ filtered water and were saturated with appropriate gases before dissolution of the solute to avoid its volatilization. All the experiments were carried out at ambient temperature (25 °C).

The ${}^{\bullet}OH$ reaction was carried out in $N_2O$-saturated solutions where $e_{aq}^{-}$ are quantitatively converted into ${}^{\bullet}OH$ radicals (reaction 2). The peroxyl radicals were generated using solutions saturated with $N_2O/O_2$ (4:1 v/v) commercially available mixtures (reactions 3 and 4). Mixtures of other $N_2O/O_2$ ratios were prepared by using a gas mixing device supplied by Eureka (Pune). The study of $O^{\bullet-}$ reaction was carried out in $N_2O$-saturated solutions at pH = 13 using 0.1 M NaOH. Under these basic conditions, the OH radical essentially exists as $O^{\bullet-}$ ($OH \rightarrow H^{+} + O^{\bullet-}$, p$K$ = 11.9).

The reactions of $SO_4^{\bullet-}$ in pulse radiolysis were studied in $N_2$-saturated solutions containing $K_2S_2O_8$ (15 mM) and *tert*-butyl alcohol (0.2 M). Under these conditions, the ${}^{\bullet}OH$ radicals are scavenged by *tert*-butyl alcohol ($(CH_3)_3COH + {}^{\bullet}OH \rightarrow (CH_3)_2{}^{\bullet}CH_2COH + H_2O$), and $e_{aq}^{-}$ ($k = 1 \times 10^{10}$ M$^{-1}$ s$^{-1}$) and H ($k = 2.5 \times 10^{7}$ M$^{-1}$ s$^{-1}$) react quantitatively with $S_2O_8^{2-}$ to give the $SO_4^{\bullet-}$ radicals.

$$e_{aq}^{-}(H) + S_2O_8^{2-} \rightarrow SO_4^{\bullet-} + SO_4^{2-}(HSO_4^{-}) \qquad (5)$$

**(B) Irradiations.** The pulse radiolysis experiments were carried out using high-energy electron pulses (7 MeV, 50 ns) from the LINAC facility at the Bhabha Atomic Research Centre, Mumbai, and the details of this facility have been described elsewhere.[18] Thiocyanate dosimetry was used for determining the dose rate. An aerated aqueous solution of KSCN (10 mM) was used for monitoring the dose delivered per pulse assuming $G\epsilon_{500} = 2152$ M$^{-1}$ cm$^{-1}$ per 100 eV for the transient $(SCN)_2^{\bullet-}$. In the reaction of OH radicals in the presence of oxygen, the dose per pulse was maintained at 600−700 rad to minimize the contribution from the bimolecular decay of the intermediates. Otherwise, the dose rate was kept at 1−1.5 krad per pulse. The transient absorption with time was recorded on a storage oscilloscope interfaced to a computer for kinetic analysis.[19] The steady-state experiments were performed using a $^{60}Co$ $\gamma$-source and its dose rate, determined by the Fricke dosimeter, was 2.8 krad min$^{-1}$.

**TABLE 1: Second-Order Rate Constants ($k/10^9$ M$^{-1}$ s$^{-1}$), Absorption Maxima ($\lambda_{max}$/nm) and Molar Absorptivities ($\epsilon$/M$^{-1}$ cm$^{-1}$) Obtained in the Reactions of ${}^{\bullet}OH$, $O^{\bullet-}$, and $SO_4^{\bullet-}$ with Cresols and Halotoluenes**

| | ${}^{\bullet}OH$ | | | $SO_4^{\bullet-}$ | | $O^{\bullet-}$ | |
|---|---|---|---|---|---|---|---|
| compound | $k$ | $\lambda_{max}$ | $\epsilon$ | $k$ | $\lambda_{max}$ | $k$ | $\lambda_{max}$ |
| 2-cresol | 12.0 | 295 | 3060 | 3.4[b] | 290, 380−400 | 2.3 | 360 |
| 3-cresol | 10.0 | 325 | 4970 | 3.8 | 290, 390 | 2.4 | 315, 390 |
| 4-cresol | 9.20 | 305 | 4210 | 6.1 | 290, 390 | 2.1 | 315, 390 |
| 2-chlorotoluene[a] | 6.50 | 325 | 3600 | 1.7 | 320 | | n.d[c] |
| 3-chlorotoluene | 3.50 | 330 | 4200 | 0.9 | 325 | | n.d |
| 4-chlorotoluene | 5.50 | 310 | 4000 | 1.1 | 270, 315 | | n.d |
| 2-bromotoluene | 1.70 | 330 | 3450 | 2.3 | 315, 435 | | n.d |
| 3-bromotoluene | 4.90 | 330 | 5200 | 1.7 | 320 | | n.d |
| 4-bromotoluene | 2.90 | 315 | 3700 | 1.0 | 275, 325 | | n.d |

[a] The values for halotoluenes are taken from refs 9a and 10a. [b] Determined by laser flash photolysis technique. [c] Not determined.

The laser flash photolysis experiments were carried out using a home-built setup at the Tata Institute of Fundamental Research, Mumbai. This setup consisted of an excimer laser with a KrF fill ($\lambda = 248$ nm) as the excitation and a xenon lamp with a monochromator as the monitoring light sources. The transient signal, detected by a photomultiplier, was digitized by a Biomation waveform recorder (Model 8100 Gould Inc.) and then transferred to a minicomputer. Signal averaging of typically 5−10 traces was done to improve the signal-to-noise ratio. The aqueous solution of the reactants, deoxygenated by bubbling with nitrogen gas, was flowed through a quartz cuvette of 1 cm path length using a peristaltic pump in order to avoid accumulation of reaction products during the run.

**(C) Estimation of Reaction Products.** The HPLC system (Series 10 Liquid Chromatograph) from Perkin-Elmer coupled to a LC-235 photodiode array detector and a reverse phase Nucleosil C-18 column (250 mm, 5 $\mu$m) or a Lichrosphere column (125 mm, 5 $\mu$m) were used for the determination of the product yields. The column effluent was monitored at 260 nm in the case of cresols and 280 nm in chlorotoluenes. The solvent employed was 40% acetonitrile in water with a flow rate of 1 mL min$^{-1}$. The standards: 2,3-, 2,6-, 3,4-, and 3,5-dihydroxytoluenes were obtained from Fluka. The products obtained from irradiation were identified from their retention times and UV spectra. The yields were determined by comparing the peak areas of the products with those obtained for the standards under identical experimental conditions and the $G$ values were estimated from the yield versus dose plots.

## 3. Results and Discussion

**(A) Kinetics.** *(i) Reactions of ${}^{\bullet}OH$ and $O^{\bullet-}$ with Cresols.* The rates of reactions of ${}^{\bullet}OH$ with 2-, 3-, and 4-cresols were studied by measuring the transient absorption at the corresponding $\lambda_{max}$ values (295−325 nm) from pulse radiolysis of $N_2O$-saturated solutions. The rates were found to depend linearly on solute concentration, and the second-order rate constants evaluated from the plots of $k_{obs}$ versus [solute] (0.2−1 mM) are given in Table 1. Also listed in this table are the corresponding rate constants reported[9a,10a] for bromo- and chlorotoluenes by us earlier. The observed rates for cresols are the highest ($k \approx 1 \times 10^{10}$ M$^{-1}$ s$^{-1}$) among those found for disubstituted benzenes (compare these with those found for halotoluenes ($1.5-1.7 \times 10^{9}$ M$^{-1}$ s$^{-1}$) shown in Table 1). Since the OH radical is electrophilic in nature, its high reactivity toward cresols can be attributed to the electron-donating nature of the $-$OH and $-CH_3$ groups as compared to $-$Br or $-$Cl in halotoluenes. The rates with cresols represent the upper limit of diffusion-controlled reaction. This is also in accord with our earlier finding[8] of the additive nature of activation effects of $-CH_3$ and $-$Cl groups of chlorotoluenes.

The rate constants ($k \approx 2.4 \times 10^{9}$ M$^{-1}$ s$^{-1}$ ) measured by monitoring the absorption of the transients formed at $\lambda_{max}$ (390$-$410 nm) for the reaction of $O^{\bullet-}$ with cresols are lower by a factor of 4 than those found in $^{\bullet}$OH reaction (Table 1). This reduction in reactivity of $O^{\bullet-}$ is due to the electrostatic repulsion following the deprotonation of cresols at the pH 13 employed in our experiments. (p$K_a$(2-cresol) = 10.28 and p$K_a$(4-cresol) = 10.17).[7]

*(ii) Reaction of $SO_4^{\bullet-}$.* The rate constants for $SO_4^{\bullet-}$ reaction with 3- and 4-cresols by pulse radiolysis were determined from the transient absorption maxima at 295 and 410 nm, respectively, rather than from the decay of $SO_4^{\bullet-}$ at 460 nm ($\epsilon$ = 1100 M$^{-1}$ cm$^{-1}$). This enabled us to obtain traces with high signal-to-noise ratios. The rate constants determined from $k_{obs}$ versus [solute] for 3- and 4-cresols are $3.8 \times 10^{9}$ and $6.2 \times 10^{9}$ M$^{-1}$ s$^{-1}$, respectively.

$SO_4^{\bullet-}$ was also produced using the 248 nm excimer laser by photolysis of $S_2O_8^{2-}$ (energy per pulse = 60 mJ, pulse width $\approx$ 20 ns). Using $N_2$, saturated solutions of 50 mM $S_2O_8^{2-}$ were photolyzed. This spectrum is in accord with that reported earlier for $SO_4^{\bullet-}$ by flash photolysis[16a] and pulse radiolysis[20] methods. The rate of its decay was found to be fast, and the self-reaction (reaction 6) was complete in less than 40 $\mu$s.

$$2\,SO_4^{\bullet-} \rightarrow S_2O_8^{2-} \qquad (6)$$

The first half-life for its decay was found to be about 3.6 $\mu$s. Assuming a $\epsilon_{460}$ value of 1100 M$^{-1}$ cm$^{-1}$, the estimated rate constant for reaction 6 is at least twice as high as those reported[16,17] by photochemical methods; but is close to the value determined by Jiang et al.[7b]

To reduce the contribution of the bimolecular decay of $SO_4^{\bullet-}$ and to have pseudounimolecular reaction conditions with the solute, the concentration of $S_2O_8^{2-}$ was maintained at 5 mM in further experiments where [$SO_4^{\bullet-}$] generated was $7.5 \times 10^{-5}$ M. For kinetic studies, this concentration of $S_2O_8^{2-}$ and [cresol] in the range 0.1$-$0.3 mM was found to be optimum. The rate constant for photochemical reaction of $SO_4^{\bullet-}$ with 2-cresol was determined to be $3.4 \times 10^{9}$ M$^{-1}$ s$^{-1}$ from the linear dependence of the rate with [2-cresol]. The $k$ values for $SO_4^{\bullet-}$ reaction with isomers of cresols ($(3-6) \times 10^{9}$ M$^{-1}$ s$^{-1}$) are lower than those found for the $^{\bullet}$OH reaction ($1 \times 10^{10}$ M$^{-1}$ s$^{-1}$), indicating that $SO_4^{\bullet-}$ is more selective. Such a selectivity in $SO_4^{\bullet-}$ reaction was also seen by Neta et al.[21] in monosubstituted benzenes ($\rho^{+} = -2.5$) and by us[10] in di- and trisubstituted benzenes ($\rho^{+} = -1.6$).

**(B) Transient Absorption Spectra.** (*i*) *Reaction of $^{\bullet}$OH and $O^{\bullet-}$: Deoxygenated Solutions of Cresols.* The transient absorption spectra obtained on pulsing $N_2O$-saturated solutions containing 1 mM 2-, 3-, or 4-cresol are given in Figure 1A. These spectra exhibited peaks at 295 nm in the case of 2-cresol and at 325 and 305 nm for meta and para-isomers, respectively. The time-resolved spectra revealed no further spectral changes (not shown in figure) except the bimolecular decay of the intermediates on longer time scale.

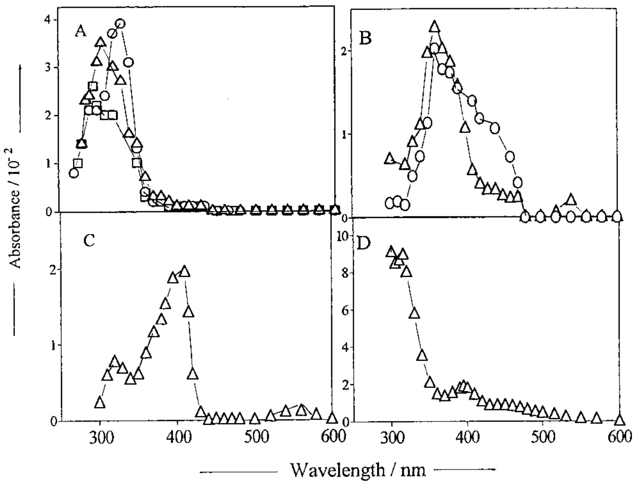
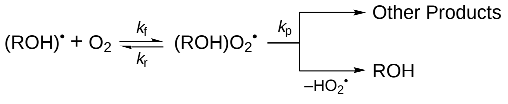


**Figure 1.** (A) Transient absorption spectra recorded at 2 $\mu$s after the pulse obtained in the reaction of OH with (△) 2-, (○) 3-, and (□) 4-cresols. Time-resolved transient spectra obtained in the reaction of $O^{\bullet-}$ with (B) 2-, (C) 3-, and (D) 4-cresols at 2.5 $\mu$s (△) and 18 $\mu$s (○) after the pulse. Dose per pulse = 1.5 krad; pH = 13, [solute] = $10^{-3}$ M.

The transient absorption spectra measured in $N_2O$-saturated basic solutions (pH = 13) of cresols after completion of reaction (2.5 $\mu$s) are different for the three isomers. The spectrum obtained with 2-cresol has a single intense peak around 360 nm and a very weak absorption above 500 nm (Figure 1B$-$D). The spectra in the case of 3- and 4-cresols have, however, two distinct peaks around 310$-$315 and 380$-$390 nm. While the intensity of the 390 nm peak in 4-cresol is comparable to the corresponding peak observed with the *m* isomer, the intensity of the former (315 nm) was enhanced 5-fold. The time-resolved absorption spectra have shown the usual bimolecular decay of the transients formed in 3- and 4-cresols (not shown in figure), whereas a clear increase in absorption in the region of 410$-$440 nm for 2-cresol was observed. The rate of this increase at 410 nm estimated from the time-resolved spectrum (Figure 1B) is about $7 \times 10^{5}$ s$^{-1}$.

(*ii*) *Oxygenated Solutions.* As pointed out in the Introduction section, the addition of molecular oxygen to carbon-centered radicals in aqueous solutions is usually fast, with rates close to diffusion-controlled. The cyclohexadienyl radical, for example, reacts[2] very rapidly ($k = 3.1 \times 10^{9}$ M$^{-1}$ s$^{-1}$), which is followed by rapid elimination of $HO_2^{\bullet}$ with other competing processes. On the other hand, its addition to OH adducts of benzene and its derivatives was reported[2b] to be slower and reversible (reaction 7).



(7)

By monitoring the decay of absorption of OH adducts in the presence of oxygen at lower doses, Fang et al.[3] have determined the rate constants using eq 8.

$$k_{obs} = k_f[O_2] + k_r \qquad (8)$$

They have shown that the forward ($k_f$) and backward ($k_r$) rates depend on the nature of the substituent, with $k_f$ values lying between $8 \times 10^{8}$ M$^{-1}$ s$^{-1}$ for anisole and $1.6 \times 10^{7}$ M$^{-1}$ s$^{-1}$ for terephthalate ion and the corresponding values of $k_r$ between $7.5 \times 10^{4}$ and $0.35 \times 10^{4}$ s$^{-1}$.

In Figure 2 is given the spectrum recorded in oxygenated solutions of 3-chlorotoluene. The time-resolved spectra shown in this figure clearly indicate the formation of peroxyl radical,

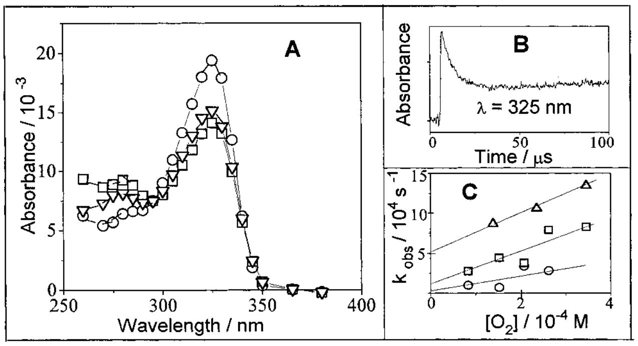


**Figure 2.** (A) Time-resolved absorption spectra obtained from pulse radiolysis of $N_2O/O_2$ (4:1 v/v) saturated solutions of 3-chlorotoluene at 3 (○), 40 (▽), and 90 $\mu$s (□). Dose per pulse = 600−700 rad. (B) Decay trace at 325 nm in the presence of $O_2$ in 3-cresol. (C) Plot of $k_{obs}$ as a function of $[O_2]$ in (○) 2- and (△) 3-chlorotoluenes and (□) 3-cresol.

**TABLE 2: Rate Constants for Forward ($k_f/10^8$ M$^{-1}$ s$^{-1}$) and Reverse ($k_r/10^4$ s$^{-1}$) Reactions and Stability Constants ($K/10^4$ M$^{-1}$) Obtained in the Reactions of Oxygen with OH Adducts of Some Substituted Benzenes**[a]

| substrate | $k_f$ | $k_r$ | $K$ |
|---|---|---|---|
| toluene | 4.80 | 7.50 | 0.64 |
| chlorobenzene | 2.60 | 5.50 | 0.47 |
| 2-chlorotoluene | 1.00 | 0.25 | 4.00 |
| 3-chlorotoluene | 2.70 | 5.00 | 0.53 |
| 2-cresol | 2.70 | 0.50 | 5.44 |
| 3-cresol | 2.00 | 1.20 | 1.73 |
| 4-cresol | 2.10 | 0.30 | 3.50 |

[a] The values for toluene and chlorobenzene are taken from ref 3.

as can be seen from the increase in absorption at 275 nm with a corresponding decrease in absorption intensity at 330 nm. The decay of absorption in the case of 3-cresol in the presence of 20% oxygen is depicted in the inset of Figure 2. The decay of the OH adducts of 3-cresol was found to be faster than that observed for 3-chlorotoluene.

The plots of $k_{obs}$ determined from such traces as a function of $[O_2]$ in the range (0.8−3.5) × $10^4$ M for chlorotoluenes and cresols are shown in Figure 2C. The $k_f$, $k_r$, and $K(k_f/k_r)$ values obtained from these plots are listed in Table 2. In this table are also included the values reported[3] for toluene and chlorobenzene. Since the variation measured in the $k_f$ and $k_r$ values is large with 4-chlorotoluene, they are not included in this table. The rates of oxygen addition ($k_f = (1-4.8) \times 10^8$ M$^{-1}$ s$^{-1}$) with toluene, chlorobenzene, chlorotoluene, and cresols are in general higher. However, the rates for the reverse reaction ($k_r$) in cresols are lower by 3−4 times than those observed for the rest, the exception being 2-chlorotoluene. Thus, the stability constants ($K$) for 2-chlorotoluene and 2- and 4 cresols are higher, suggesting that the product formation seems to compete with the reverse reaction 7. As a consequence, the estimated $k_f$ and $k_r$ values based on eq 8 may be somewhat higher by about 10−15% than the actual values. Nevertheless, they still provide us with a guideline to compare the relative reactivities of oxygen with these isomers.

*(iii) Reaction of $SO_4^{\bullet-}$.* The absorption spectra of the intermediates formed in the reaction of $SO_4^{\bullet-}$ with 2-, 3-, and 4-cresols were also recorded in the wavelength region 250−500 nm, and the fully developed spectra obtained at 2 $\mu$s after the pulse are shown in Figure 3A−D. It can be clearly seen that all the three spectra are more or less similar, with peaks centered around 290 and 390−400 nm. While the intensities of the peaks at 290 nm observed in the spectra with 2- and 4-cresols are nearly the same, its intensity in 3-cresol was reduced with a corresponding increase in the intensity of the peak at the higher wavelength. For instance, the corresponding ratios are 2.5−3 for 2- and 4-cresols, whereas it is only 1.2 in the case of 3-cresol. Furthermore, a slow rate of increase in absorption was observed in the region 330−340 nm, as can be seen from the time-resolved spectra (Figure 3A−D), obtained at 40 $\mu$s after the pulse in all three isomers.

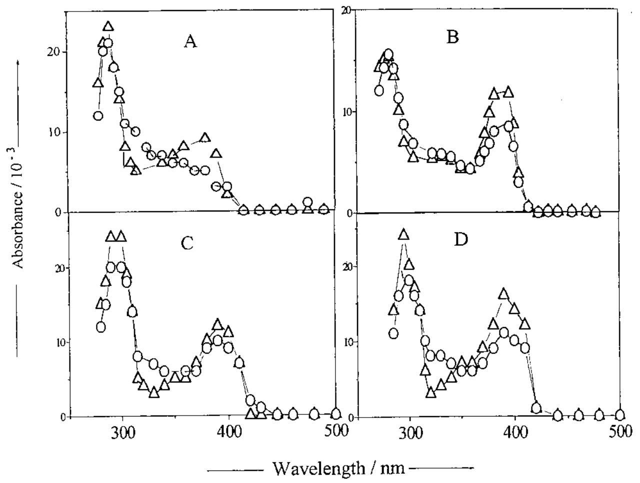


**Figure 3.** (A) Time-resolved transient absorption spectra obtained in $SO_4^{\bullet-}$ reaction with (A) 2-, (B) 3-, and (C) 4-cresols at pH = 7. (D) 4-cresol at pH = 9 at 2 $\mu$s (△) and 40 $\mu$s (○) after the pulse. Dose per pulse = 1.4 krad, [solute] = $10^{-3}$ M.

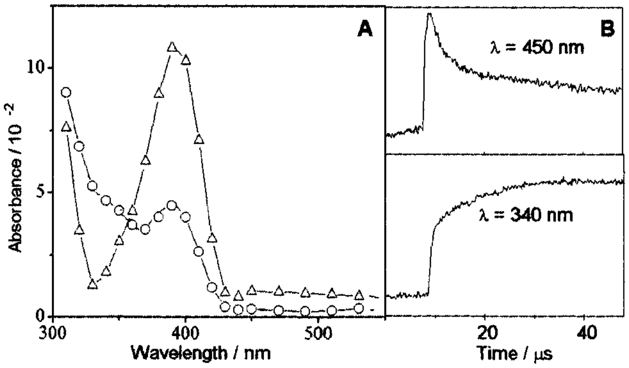


**Figure 4.** (A) Time-resolved absorption spectra obtained in $SO_4^{\bullet-}$ reaction of with 4-cresol by laser flash photolysis at 2 $\mu$s (△) and 40 $\mu$s (○) after the flash. Excitation 248 nm; energy per pulse = 60 mJ; pH = 7, [solute] = 2 × $10^{-4}$ M. (B) Traces of buildup at 340 nm and decay at 450 nm measured by laser flash photolysis in 4-cresol.

The spectrum recorded in $SO_4^{\bullet-}$ reaction with 4-cresol by flash photolysis in the range 310−500 nm is shown in Figure 4. Due to the low intensity of the analyzing Xe lamp and poor response of PMT, measurements could not be carried out below 310 nm. Hence, the peak at 290 nm in the spectrum measured by pulse radiolysis was not seen. Otherwise, the spectrum is identical with that observed in pulse radiolysis (Figure 3C), indicating that the same transient species were formed in both the methods. As in the case of pulse radiolysis measurements, the formation of another species absorbing in the range 325−340 nm with an isosbestic point at ~355 nm was noticed. The first-order rate constant for the formation of this species (inset of Figure 4) was estimated to be 1.2 × $10^5$ s$^{-1}$. This rate, however, could not be evaluated from the pulse radiolysis spectrum due to low absorption values.

**(C) Product Analysis of Chlorotoluenes and Cresols.** The products formed from •OH reaction with 2-, 3-, and 4-chlorotoluenes in the presence of oxygen ($N_2O/O_2$ [4:1]) were separated by HPLC, and the chromatograms obtained for a dose of 16.8 krad are shown in Figure 5A−C. This figure also

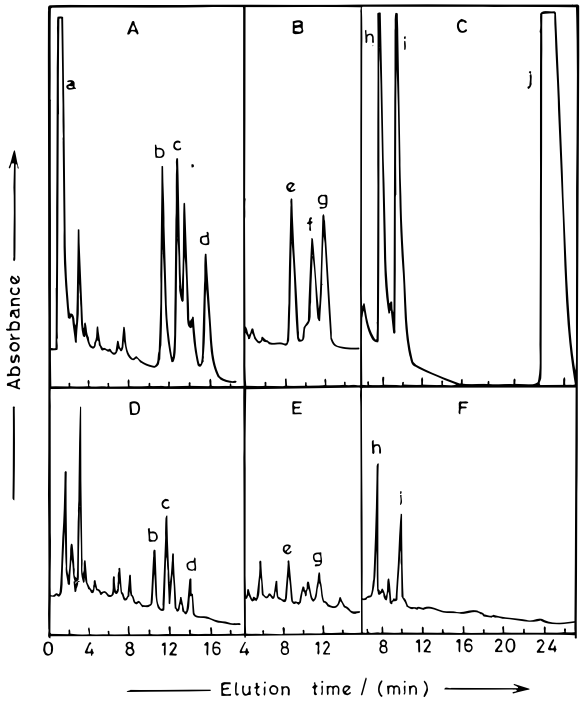
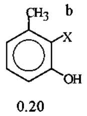
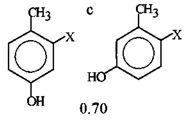
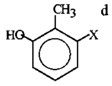
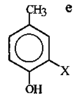
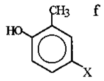
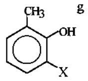
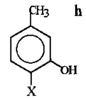
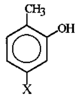


**Figure 5.** HPLC chromatograms obtained for the products formed in the reaction of OH radicals in the presence of oxidant $K_3[Fe(CN)_6]$ (A−C) and oxygen (D−F) with 2-, 3-, and 4-chlorotoluene. (dose = 16.8 krad). Peaks a: ferricyanide, b-i: isomers of hydroxychlorotoluenes, j: solute. See Table 3 for the structures of phenolic products.

contains the chromatograms obtained in deoxygenated solutions in the presence of the oxidant, 1 mM $Fe(CN)_6^{3-}$, (Figure 5D−F). The yields of the phenolic products formed in the presence of oxygen were calculated based on the $G$ values reported[10b] by us earlier in deoxygenated solutions which are listed in Table 3. While the formation of only phenolic products was observed under deoxygenated conditions, some additional products were seen in oxygenated solutions. However, the individual phenolic yields were reduced by more than 80% in the presence of oxygen.

The yields of radiation products formed by $\gamma$-radiolysis of chlorobenzene with and without oxygen have already been reported.[10c] For a comparison, we also carried out experiments with toluene under both oxygenated and deoxygenated conditions. The formation of only two products was noticed in $\gamma$-radiolysis of $N_2O$-saturated solutions of toluene containing $Fe(CN)_6^{3-}$ which were identified as 2- and 4-cresols with $G$ values of 1.7 and 0.6, respectively. Our value for the total yield of cresols ($G$(cresols) = 2.3) is less than that reported[22] earlier in $\gamma$-radiolysis of argon-saturated solutions of toluene containing 0.5 mM $Fe(CN)_6^{3-}$. What is, however, relevant for our present discussion is the lack of formation of cresols ($G$(cresols) $\leq$ 0.2) in the presence of oxygen.

**TABLE 3: Product Distribution Obtained in $\gamma$-Radiolysis of Deoxygenated and Oxygenated Solutions of Chlorotoluenes and Cresols[a]**

| Isomer | Products | | | Total Yield : %OH |
|---|---|---|---|---|
| *Ortho* | b  | c  | d  | |
| X = Cl | 0.20<br>*(1.1)* | 0.70<br>*(2.4)* | 0.14<br>*(1.3)* | 1.04 : 18%<br>*(4.80 : 86%)* |
| X = OH | 1.4<br>*(1.4)* | n.f<br>*(1.4)* | n.f | 1.40 : 25%<br>*(2.80 : 50%)* |
| *Meta* | e  | f  | g  | |
| X = Cl | 0.4<br>*(2.1)* | 0.2<br>*(2.3)* | n.f<br>*(0.9)* | 0.60 : 11%<br>*(5.30 : 95%)* |
| X = OH | 1.2<br>*(1.2)* | n.f | 1.1<br>*(1.1)* | 2.3 : 41%<br>*(2.3 : 41%)* |
| *Para* | h  |  | | |
| X = Cl | 0.3<br>*(2.5)* | 0.2<br>*(2.2)* | | 0.64 : 11%<br>*(4.7 : 84%)* |
| X = OH | 2.0<br>*(3.6)* | n.f<br>*(1.3)* | | 2.0 : 36 %<br>*(4.9 : 87%)* |

[a] The numbers are the $G$ values of the individual phenolic products formed in deoxygenated (given in parantheses) and oxygenated solutions of chlorotoluenes (X = Cl) and cresols (X = OH). The total yields are based on $G$(OH) = 5.6 per 100 eV. See HPLC chromatograms (Figures 5 and 6) for the separation of the phenolic products. n.f = not formed.

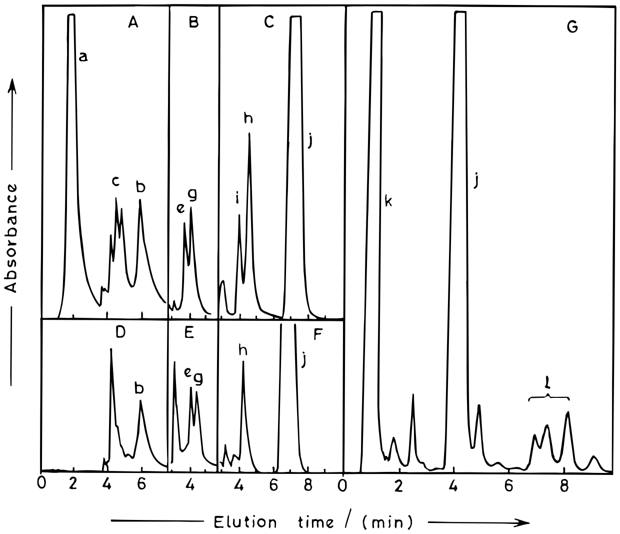
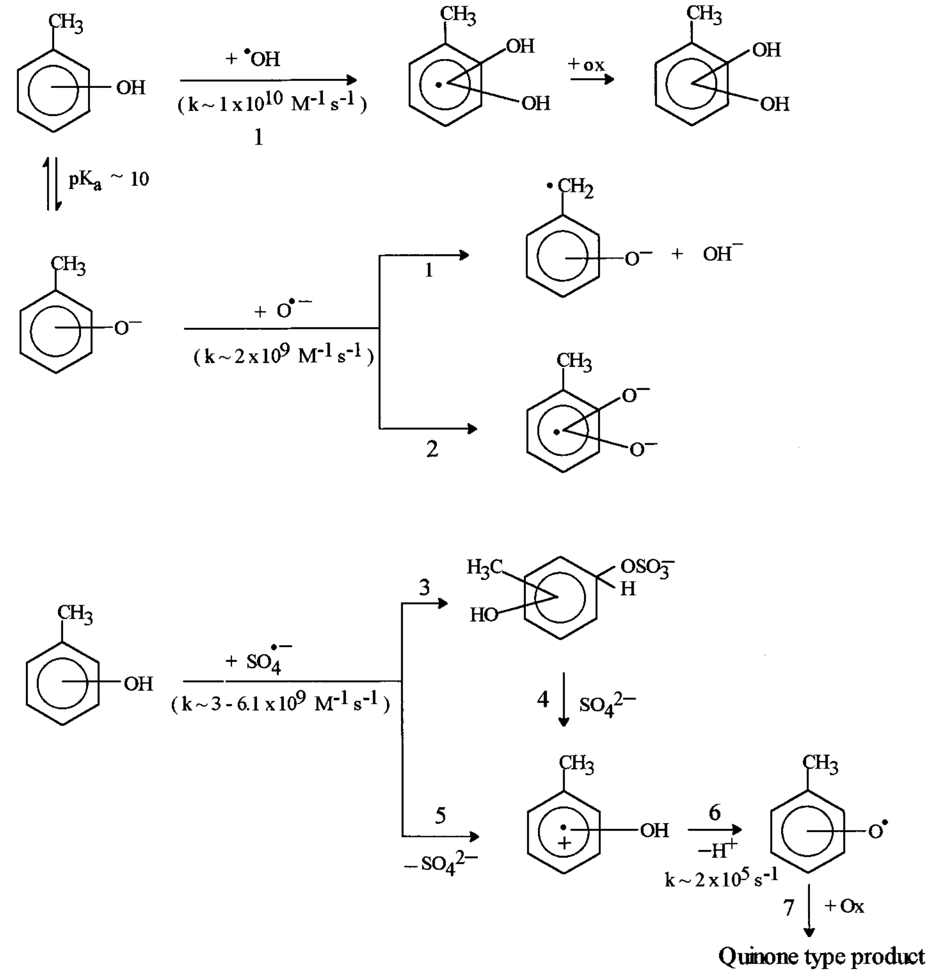


**Figure 6.** HPLC chromatograms obtained for the products formed in the reaction of OH radicals in the presence of oxidant $K_3[Fe(CN)_6$ (A−C) and oxygen (D−F) with 2-, 3-, and 4-cresols. (G) Chromatogram obtained in $SO_4^{\bullet-}$ reaction with 3-cresol. dose = 16.8 krad. Peaks a: ferricyanide, b-i: isomers of hydroxychlorotoluenes, j: solute, k: persulfate, and l: quinone type products. See Table 3 for the structures of phenolic products.

In contrast, the behavior with cresols is different from that observed for toluene and chlorotoluenes. The HPLC chromatograms obtained with 2-, 3-, and 4-cresols under both solution conditions are depicted in Figure 6A−F. As can be seen from the chromatograms recorded in deoxygenated solutions of cresols containing Fe $(CN)_6^{3-}$, two major products were formed with each isomer. In the meta isomer, the two products were identified as 2,3- and 3,4-dihydroxytoluenes (DHT) (peaks g and e in Figure 5B, respectively) from a comparison of their retention times and UV spectra with those of the standards. However, only one of the products, 2,3-DHT (peak b in Figure 5A) in 2-cresol and 3,4-DHT (peak h in Figure 5C) in the case of 4-cresol, could be identified. The retention times and the spectra of the other two unidentified peaks did not match with 3,5- or 2,6-DHT. Based on the probable site of attack, the two unidentified peaks in 2-cresol were assigned to 2,4- and 2,5-DHT (peak c in Figure 5A); similarly, the unidentified peak in 4-cresol was assigned to 2,4-DHT (peak i in Figure 5C). The $G$ values of these products were calculated by assuming that

**SCHEME 1: Mechanism for Reactions of OH, $O^{\bullet-}$, and $SO_4^{\bullet-}$ with Cresols**



their molar absorptivities are equal to that of the identified isomer. Our efforts to synthesize these two isomers (2,4- and 2,5-DHT) by the Fenton's reaction have not been successful, as a brownish black substance as reported[23] in the literature was precipitated when 6 × $10^{-3}$ M $FeSO_4 \cdot 7H_2O$ was reacted with these isomers of cresol (2 × $10^{-3}$ M) in the presence of $H_2O_2$.

The $G$ values of the phenolic products formed from cresols under different conditions are given in Table 3. The yields of 2,3- and 2,4- + 2,5-DHT formed in $N_2O$-saturated solutions of 2-cresol containing 0.5 mM Fe $(CN)_6^{3-}$ were estimated to be 1.4 each per 100 eV. The $G$ values for 3,4- and 2,3-DHT formed in the $\gamma$-radiolysis of 3-cresol under identical conditions are 1.2 and 1.1, respectively, amounting to about 41% OH. In contrast, the yields of 2,4- and 3,4-DHT ($G$(2,4-DHT) = 1.3 and $G$(3,4-DHT) = 3.6) could account for near complete material balance (87% OH) in the case of 4-cresol. In oxygenated solutions of 2- and 4-cresols some dihydroxytoluenes were not at all formed or their yields reduced, while they remained unaffected in the case of the meta isomer. For instance, the formation of 2,4- and 2,5-DHT in 2-cresol and 2,4-DHT in the para isomer was not observed.

To evaluate the directing effects of −OH and $-CH_3$ groups for OH attack, we employed the procedure developed by Chen and Schuler[11d] in the case of biphenyl and later used by us[10b] for chlorotoluenes. Due to lack of material balance of products in the case of 2- and 3-cresols, the analysis was limited to the para isomer and the partial and relative rates with respect to benzene are given in Figure 7 along with that for 4-chlorotoluene. The relative rates in 4-cresol at the ortho and meta positions to −OH are 2.3 and 0.8 compared to the corresponding values of 1.3 and 1.18 in 4-chlorotoluene. This result is in accord with the stronger activation of ortho and deactivation of meta positions by the −OH group.

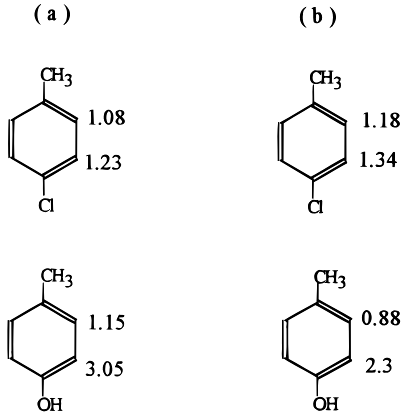
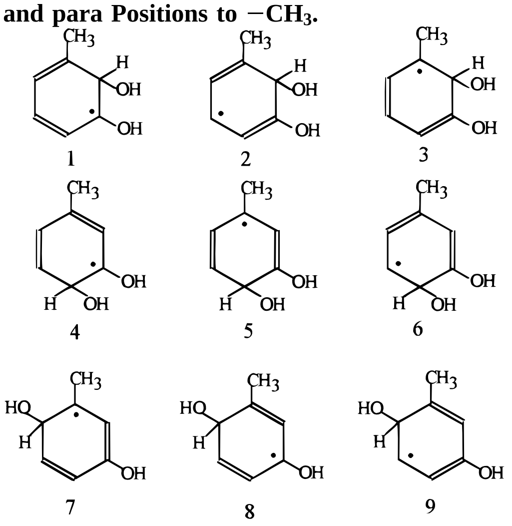


**Figure 7.** (a) The partial ($10^9$ $M^{-1}$ $s^{-1}$) and (b) the relative rate constants with respect to benzene for 4-chlorotoluene and 4-cresol.

**(D) Reaction Mechanism.** *(i) Deoxygenated Solutions of Cresols.* Since the extent of OH attack at different positions is determined by the nature of the substituent on the benzene ring, the observed spectra represent the weighted average of isomeric OH adducts of cresols formed from the addition of the OH radical to the benzene ring (reaction 1, Scheme 1). A comparison of the transient absorption spectra measured with cresols shows a red shift in the case of the meta isomer by about 20−30 nm from its *o* and *p* isomers. This is also reflected in the more intense absorption measured for 3-cresol and the order

**SCHEME 2: Different Mesomeric Structures of OH Adducts of 3-Cresol Formed from •OH Attack at the ortho and para Positions to $-CH_3$.**



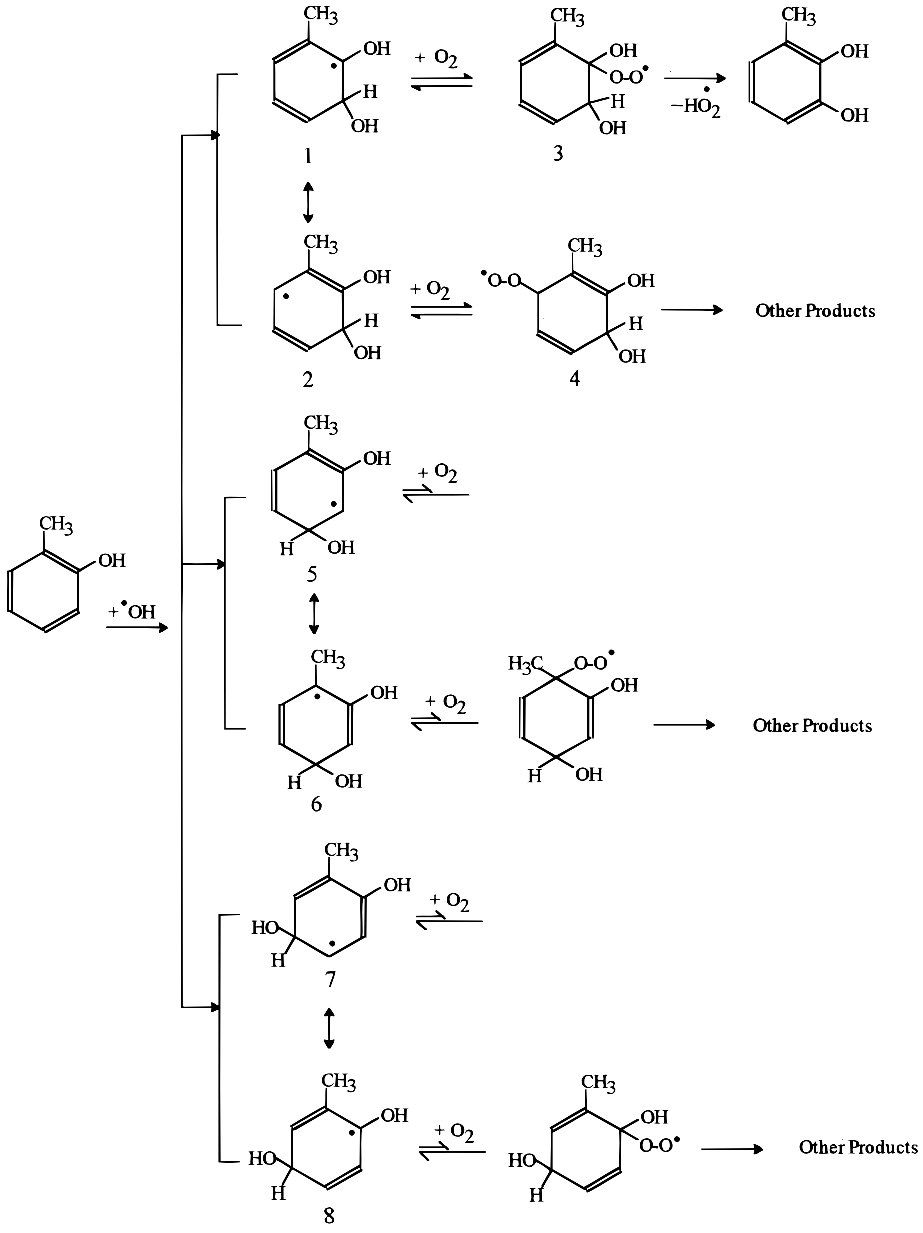
found for the molar absorptivities *m* > *p* > *o*. Such a shift was also observed for the *m* isomers of chlorotoluenes[10b] and xylenes with $\lambda_{max}$ at 325−330 nm compared to their *p* isomers ($\lambda_{max}$ = 310 nm). This behavior was attributed to the stabilization of the excited states of meta-substituted isomeric hydroxycyclohexadienyl radical. The general •OH, $O^{\bullet-}$, and $SO_4^{\bullet-}$ reaction mechanism with creosls is depicted in Scheme 1.

For example, the possible resonance structures of the hydroxycyclohexadienyl radicals (structures 1−9) formed from addition of •OH to 3-cresol are given in Scheme 2. The structures from the attack of •OH at the ortho and para positions to $-CH_3$ only are shown. The unpaired electron spin in the OH adducts of the *m* isomer are delocalized on both −OH and $-CH_3$ substituents unlike in the case of its *o* and *p* isomers. This results in the better stabilization of the meta OH adducts relative to the corresponding adducts formed in *o* and *p* isomers.

Under the basic conditions (pH = 13) employed in the reaction of $O^{\bullet-}$, cresols exist as monoanions (p$K_a$ = 10−11). $O^{\bullet-}$ being a nucleophile, its addition to the ring is not likely. The probable reaction channel is, therefore, the abstraction of H from the $-CH_3$ group, leading to the formation of substituted benzyl radicals (reaction 2, Scheme 1).

From the $\rho^+$ value of −2.4 found with some substituted benzenes, Neta et al.[21] suggested that the $SO_4^{\bullet-}$ reaction

**SCHEME 3: Reaction Sequence of Oxygen Addition to Different OH Adducts of 2-Cresol**



mechanism proceeds by a direct electron transfer from the benzene ring to $SO_4^{\bullet-}$. It has been shown by us in our earlier work[9,10] with halobenzenes ($\rho^+ = -1.2$) and halotoluenes ($\rho^+ = -1.6$) that the reaction may occur both by addition/elimination (reaction 4) and by outersphere electron-transfer (reaction 5). The lifetime of $SO_4^{\bullet-}$ adduct to benzenes is known[24] to be $\leq 100$ ns. With the electron-donating substituents $-CH_3$ and $-OH$, the hydrolysis rate of the $SO_4^{\bullet-}$ adducts should be still higher, and the reaction must be complete within the pulse width (50 ns) of our experiment.

The transients absorbing at 290 and around 400 nm in the reaction of $SO_4^{\bullet-}$ with cresols are assigned to the radical cation based on the similarity of the spectra reported[10] by us in the $SO_4^{\bullet-}$ reaction in the case of 3- and 4-chloroanisoles ($\lambda_{max} = 290$ and 450 nm), though the second peak in these systems is at a higher wavelength (450 nm). This assignment is substantiated by the observed faster decay of the transient absorption at 290 and 390 nm in 4-cresol when $SO_4^{\bullet-}$ reaction was carried out at pH = 9 (Figure 3D). As pointed earlier (cf. section 3B (iii) $SO_4^{\bullet-}$ reaction), this decay was manifest by an increase in absorption in the region 320−340 nm whose rate was estimated as $1.2 \times 10^5$ $s^{-1}$ from laser flash photolysis of 4-cresol in neutral solutions. This transformation reaction must, then, be due to the formation of substituted phenoxyl radical by deprotonation of the radical cation (reaction 6, Scheme 1). Furthermore, some other radiation products in addition to phenolic products were formed in $SO_4^{\bullet-}$ reaction with cresols under $\gamma$-radiolysis. This is evident from the HPLC chromatogram depicted in Figure 6G for 3-cresol, where the formation of quinone type products (peaks l in Figure 5G) eluting after the phenolic products should result from the oxidation of phenoxyl radical (reaction 7).

The phenolic yields formed in the isomers of chlorotoluenes and cresols are in accord with the usual activation and deactivation effects of −Cl and −OH groups. For instance, the lack of formation of 2,6-DHT and reduction in the yield of 2,4-DHT in the case of 2-cresol relative to the corresponding phenols formed in chlorotoluene is due to the deactivation of meta position of the −OH group. Similar deactivation of the meta and activation of the para positions was responsible for reduction in the yield of 2,4- and enhancement in 3,4-DHT yields in the case of 4-cresol. An exception to this is the behavior of 3-cresol, where a lower yield of 3,6-DHT and lack of formation of phenols formed from the attack of −OH at the para position were noticed.

*(ii) Oxygenated Solutions of Chlorotoluenes and Cresols.* It is known[1−3] that the phenolic products can be formed by $HO_2^{\bullet}$ elimination from only 1,3-cyclohexadienyl peroxyl radicals, whereas 1,4-type radicals result in endoperoxidic products. The relatively larger phenolic yields observed in the case of cresols suggest that the rates of $HO_2^{\bullet}$ elimination and other product forming reactions are higher than in the case of 3- and 4-chlorotoluenes. This finding is further substantiated by the larger values of the stability constants, $K$ (Table 2), observed in the case of cresols. The lower yields of phenolic products in 3- and 4-chlorotoluenes are possibly due to relatively higher $k_r$ and lower $k_p$ values. In other words, the reverse reaction of the equilibrium probably predominates over the product formation in these compounds. This means that a major fraction of 1,3-type structures are ultimately converted into 1,4-cyclohexadienyl type structures.

An interesting observation is that only those dihydroxytoluenes with −OH groups ortho to each other were formed in oxygenated solutions of cresols. The formation of such isomers of cresols is possible only from 1,3-type peroxyl radicals when the radical site is localized at the carbon carrying the −OH group. Scheme 3 depicts the sequence of oxygen addition reactions with 2-cresol, as an example, wherein the formation of 2,3-DHT occurs from the peroxyl radical **3**. The other peroxyl radical **4** formed from the OH adduct **2** is of 1,4-type, resulting in other products. The lack of formation of 2,4- and 2,5-DHT in 2-cresol is because of the fact that the radical sites in 1,3-type OH adducts (structures 5−8) are not located at the *tertiary* center.

## Conclusions

The intermediates in the reactions of $^{\bullet}OH$, $O^{\bullet-}$, and $SO_4^{\bullet-}$ with cresols are formed from addition, H-abstraction, and electron transfer. Oxygen is relatively more reactive with OH adducts of cresols than those of chlorotoluenes. The addition of oxygen to 1,3-type OH adducts of cresols occur at the carbon substituted by the OH group. This study demonstrates the usefulness of radiation chemical methods in obtaining information on peroxyl radical chemistry of chlorotoluenes and cresols.

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