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The reactions of $\cdot\text{OH}$, $\text{O}^{\cdot-}$ and N_3^{\cdot} with chloro- and hydroxy-anilines were studied by pulse radiolysis. The rates of the OH radical reaction are higher ($k \sim 5 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) than those found for the $\text{O}^{\cdot-}$ and N_3^{\cdot} reactions ($k \sim 2 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$). Neither the position of the substituent nor the introduction of an additional Cl to monochloroanilines has any significant effect on the rates of the $\cdot\text{OH}$ reaction. The intermediates formed in all the aniline derivatives studied herein have λ_{max} values around 310–320 and 350–380 nm. The OH radical reacts both by addition and direct H abstraction giving rise to OH adducts (350–380 nm) and anilino radicals (310–320 nm). The extent of these two reactions depends on the position of the substituent, the former being more predominant in the *meta* than in the *ortho* and *para* isomers. The initially-formed OH adducts subsequently undergo dehydration, leading to anilino radicals in the case of chloroanilines and phenoxy radicals with hydroxyanilines. The OH attack at the carbon bonded to Cl in all three monochloroanilines is not significant ($\leq 15\%$). Semi-empirical quantum calculations using the PM3 method were carried out to evaluate the possible sites of the OH radical attack. The charge distribution and the heats of formation data reveal that the $\cdot\text{OH}$ attack extends over more than one carbon center. The relative stabilities of the isomeric OH adducts formed from the attack at the unsubstituted carbons of chloro- and hydroxy-anilines are nearly the same, their respective heats of formation being approximately -70 and -230 kJ mol^{-1} .

Introduction

The radiation chemical oxidation of benzene and its mono-substituted derivatives by the OH radical has been widely studied [see ref. 1 (for compilation of rate constants) and the radiation chemical research literature (available at <http://www.rcdc.nd.edu>)]. Among the monosubstituted benzenes, the reactions of the OH radical with aniline,^{2–7} anisole,^{8–10} phenol,^{11–13} and toluene^{14,15} have been extensively studied and its reaction mechanism with these derivatives has been well established. The interest in these studies arises from the several advantages the radiation chemical methods offer: (i) a variety of reactive radicals ($\cdot\text{OH}$, $\text{e}_{\text{aq}}^{\cdot-}$, N_3^{\cdot} , $\text{SO}_4^{\cdot-}$ etc.) with the precise knowledge of their yields can be generated in aqueous solution; (ii) low concentrations ($\leq 10^{-3} \text{ mol dm}^{-3}$) of solute—the normal solubility limit of organic and biomolecules—can be employed; (iii) it is a clean source for the generation of the OH radical¹⁶ as compared to other methods of its production (e.g., Fenton reaction or photolysis); and (iv) the OH radical, being a weak electrophile,¹⁷ serves as a good model for examining the structure–reactivity relationship. Thus, the pulse radiolysis technique, combined with product distribution¹⁸ studies under steady state conditions, has provided valuable information on the reactivities, the spectral nature of the intermediates and the redox chemistry of OH adducts of benzene and its derivatives. Because of its specificity, von Sonntag and co-workers¹⁹ have recently suggested the use of the aromatic hydroxylation reaction as a probe for the OH radical in biological systems.

The main reaction pathway for the $\cdot\text{OH}$ reaction with benzene is by its addition to the ring, leading to the formation of hydroxycyclohexadienyl radicals. H abstraction is a

competing reaction with derivatives containing groups like NH_2 , OH , or CH_3 , the extent of this reaction being dependent on the substituent. Because of the acidic nature of H in NH_2 , aniline undergoes the H abstraction reaction to give the anilino radical more readily than phenol or toluene generates phenoxy or benzyl radicals, respectively. Moreover, the anilino ($\lambda_{\text{max}} = 310\text{--}320 \text{ nm}$) and the OH adduct ($\lambda_{\text{max}} = 350\text{--}370 \text{ nm}$) radicals of aniline are easily distinguished by their distinctive absorption spectra. The anilino radical can be selectively generated by electron transfer reaction with the azide radical, so that the contribution of each of these in the $\cdot\text{OH}$ reaction could be measured. For example, Qin *et al.*² have used the N_3^{\cdot} reaction to produce selectively the radical cation and the anilino radical of aniline in acidic and basic media, respectively. The N_3^{\cdot} radical has very low absorption above 300 nm and thus the measurements can be done using an optical pulse radiolysis method in the UV region.

We have previously reported^{20–22} the radiation chemical oxidation of disubstituted benzenes of the type $\text{C}_6\text{H}_5\text{--}_n\text{X}_n\text{Y}$, where X is a halogen and $\text{Y} = \text{Cl}$, Br , CH_3 , CH_2Cl , CF_3 or OCH_3 . Furthermore, with chlorotoluenes and cresols, the extent of the $\cdot\text{OH}$ attack at each position was estimated. However, with other disubstituted benzenes, this was not possible due to lack of standards or difficulties in their synthesis. The electronic charge distribution and heats of formation data evaluated from theoretical methods can be used as a measure to predict the favourable sites for the $\cdot\text{OH}$ attack.

Monochloro- and hydroxy- and dichloro-anilines form an interesting class of compounds for which we wanted to determine the effect of substituents and their position on the reactivity, considering the conflicting electron donating and withdrawing effects of different substituents. In this paper, we report our study on the reactions of $\cdot\text{OH}$, $\text{O}^{\cdot-}$ and N_3^{\cdot} with 2-, 3- and 4-chloroanilines, 2,4-, 3,4- and 2,5-dichloroanilines and

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Table 1 Second-order rate constants ($10^{-9} k/\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$), absorption maxima ($\lambda_{\text{max}}/\text{nm}$) and molar extinction coefficients ($\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$) obtained in the reactions of $\cdot\text{OH}$, $\text{O}^{\cdot-}$ and N_3^{\cdot} with chloro- and dichloro-anilines

Compound	$\cdot\text{OH}$		$\text{O}^{\cdot-}$		N_3^{\cdot}		
	$10^{-9} k$	λ_{max}	$10^{-9} k$	λ_{max}	$10^{-9} k$	λ_{max}	ϵ
Aniline ^a	14.0	350	2.3	310	4.2	401	1250
Chlorobenzene ^a	5.5	325			n.d.		
2-Chloroaniline	5.0	310	1.7	310	1.8	310	2455
	—	350			n.d.	410	1120
3-Chloroaniline	n.d.	310	1.6	305	2.0	305	2450
	4.5	350	n.d.	350	n.d.	410	1230
4-Chloroaniline	5.0	315	1.4	315	1.6	315	3180
		370			1.4	420	1450
2-Chlorotoluene ^b	6.5	325			n.d.		
3-Chlorotoluene ^b	3.5	330			n.d.		
4-Chlorotoluene ^b	5.5	310			n.d.		
2,4-Dichloroaniline	3.4	320	n.d.		2.8	325	
	n.d.	360			n.d.	420	
2,5-Dichloroaniline	n.d.	320	1.7	320	1.3	315	
	4.4	360			n.d.	420	
2,6-Dichloroaniline	n.d.	320	1.6	315		n.d.	
	3.5	360					
3,4-Dichloroaniline	n.d.	320	1.7	320	1.8	320	
	5.6	380			n.d.	430	

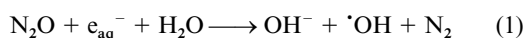
n.d., not determined. ^a Values from ref. 1. ^b Values from refs. 21 and 22.

with 2-, 3- and 4-hydroxyanilines. It is interesting to examine the differences in the reactivities between Cl- and OH-substituted aniline derivatives especially in the *meta* and *para* isomers. An attempt has been made to evaluate the directing effects of NH_2 and Cl groups on the one hand and NH_2 and OH on the other based on semi-empirical quantum chemical calculations.

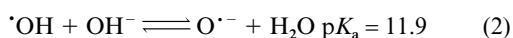
Experimental

Preparation of solutions

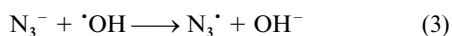
All chemicals used in this study were of high purity ($\geq 98\%$) and were commercially obtained from SISCO, CDH, SD fine-chem and Spectrochem, India. 4-Chloroaniline was used as received, while its *ortho* and *meta* isomers were distilled prior to their use. High purity N_2O gas was used for saturation. The solutions were prepared in Millipore-Milli Q filtered water and were saturated with appropriate gases before the dissolution of the solute to avoid its volatilization. All experiments were carried out at room temperature ($\sim 25^\circ\text{C}$). The concentration of the solute was usually maintained at $1 \times 10^{-3} \text{mol dm}^{-3}$ in spectral studies, and in kinetics experiments it was varied from $(0.2-1) \times 10^{-3} \text{mol dm}^{-3}$. The $\cdot\text{OH}$ reaction was carried out in N_2O -saturated solutions, where e_{aq}^- is quantitatively converted into the OH radical, reaction (1):



The study of the $\text{O}^{\cdot-}$ reaction was carried out in N_2O -saturated solutions at $\text{pH} \sim 13$ using 0.1mol dm^{-3} NaOH. Under these basic conditions, more than 90% OH radical essentially exists as $\text{O}^{\cdot-}$, reaction (2):



The reactions with the azide radicals were studied by irradiating N_2O -saturated solutions of the substrate containing NaN_3 ($2 \times 10^{-2} \text{mol dm}^{-3}$), reaction (3):



Irradiations

Pulse radiolysis experiments were carried out using high energy

electron pulses (7 MeV, 50 ns) from a linear accelerator at the Bhabha Atomic Research Centre, Mumbai; the details of the facility are published²³ elsewhere. Thiocyanate dosimetry was used to determine the dose rate. An aerated aqueous solution of $1.0 \times 10^{-2} \text{mol dm}^{-3}$ KSCN was used to measure the dose delivered per pulse by monitoring the $(\text{SCN})_2^{\cdot-}$ at 475 nm. The dose received per pulse was in the range 13–16 Gy. The transient absorption spectra were recorded, as a function of time, on a storage oscilloscope interfaced to a computer for kinetics analysis.

Results and discussion

(a) Kinetics

(i) Reactions of $\cdot\text{OH}$ and $\text{O}^{\cdot-}$. The rates of the reaction of the OH radical with mono- and di-chloroanilines in neutral N_2O -saturated solutions ($\text{pH} \sim 6.5$) were determined by measuring the rates of product formation at the absorption maxima: 310–320 or 350–380 nm. The absorption buildup measured at the two wavelengths was found to be continuous and the rates increased linearly with [solute] in the range $(0.2-0.8) \times 10^{-3} \text{mol dm}^{-3}$. The second-order rate constants evaluated from the plots of k_{obs} versus [solute] are given in Table 1 along with the values reported^{1,21,22} for related compounds. The fit of the rate data is satisfactory and the accuracy of the measured rate constant values is within $\pm 10\%$.

The average value of the rate constants measured at 350–370 nm with the three isomers of monochloroaniline is about $5 \times 10^9 \text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$, indicating that the rate was not affected by the position of the substituent. The rates of the $\cdot\text{OH}$ reaction with chloroanilines are similar to those reported for chlorobenzene²¹ and chlorotoluenes,^{20,21} but they are lower than that found for aniline. In the case of aniline, several values with $k \geq 8 \times 10^9 \text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ were reported¹ with an average value of $1.4 \times 10^{10} \text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$. Furthermore, the rate of the $\cdot\text{OH}$ reaction was not much affected when going from mono- to di-chloroanilines as is evident from the values measured in the latter ($k \sim 4.0 \times 10^9 \text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$). While the reduction in rates in the reaction with monochloroanilines compared to aniline is due to the electron-withdrawing Cl, introduction of a second Cl group seems to have only a marginal effect on the rates. In addition, the lack of influence of the substituent position on the rate among the isomers is due to the interplay between the

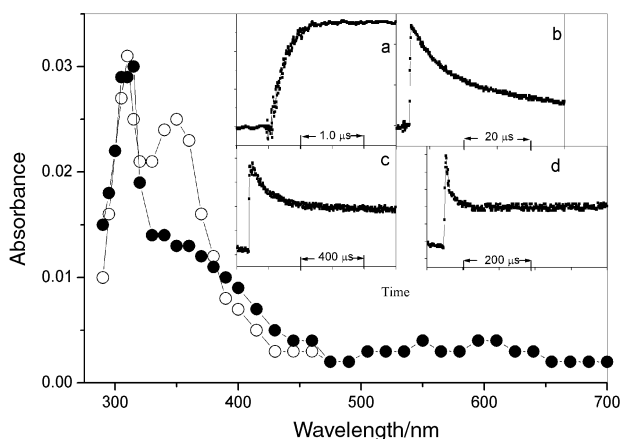


Fig. 1 Time-resolved transient absorption spectra obtained in the reaction of $\cdot\text{OH}$ with 2-chloroaniline at (○) 2 and (●) 40 μs after the pulse. Insets: (a) buildup at 310 nm; decay at (b) 350 nm; (c) 310 nm; and (d) 350 nm.

activation/deactivation effects of NH_2 , Cl and OH groups (see section c).

When N_2O -saturated basic solutions (pH \sim 13) of chloroanilines were pulse radiolysed, the rates measured at 310–315 nm for the $\text{O}^{\cdot-}$ reaction were found to be slower ($k \sim 1.5 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) than the $\cdot\text{OH}$ reaction ($k \sim 5 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$). This reduced reactivity is due to the decreased electrophilicity of the reacting radicals and the increased electrostatic repulsion between a negatively charged radical and the electron-rich aromatic ring. Such lowering of rate constants in the $\text{O}^{\cdot-}$ reaction was reported by us in earlier cases of other aromatic^{20–22} and heterocyclic compounds.²⁴

(ii) Reaction of N_3^{\cdot} . The rates for the N_3^{\cdot} reaction with the isomers of mono- and di-chloroanilines were also measured by varying the [solute] in the range $(0.2\text{--}1.0) \times 10^{-3} \text{ mol dm}^{-3}$. The rate constants are given in Table 1. In general, the rate constant values for the N_3^{\cdot} reaction with chloroanilines are lower ($k \sim 1.5 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) than for the corresponding $\cdot\text{OH}$ reaction. This is expected because the reaction pathways in the two reactions are different: *i.e.*, electron transfer *versus* addition reaction.

(b) Transient absorption spectra

(i) Reaction of $\cdot\text{OH}$. Monochloro- and hydroxy-anilines. The transient absorption spectrum recorded in the $\cdot\text{OH}$ reaction at pH 6.5 with 2-chloroaniline at 2 μs after the pulse exhibited two peaks around 310 and 350 nm as shown in Fig. 1. This figure also contains the absorption trace showing the buildup at 310 nm on 2.5 μs time scale (inset a) which is similar to that measured at 350 nm (not shown). The time-resolved absorption spectrum measured at 40 μs after the pulse shows nearly 50% decay in absorption at 350 nm with a marginal increase in intensity in the region 400–420 nm. The trace depicting this decrease is shown in inset b, Fig. 1. The rate of this decay was estimated to be $8.5 \times 10^4 \text{ s}^{-1}$. Furthermore, the traces recorded on longer time scales at 310 (1000 μs) and 350 nm (500 μs) clearly reveal that the species absorbing at 350 nm is shorter-lived (insets c and d, Fig. 1). Though the rates of the absorption buildup at the two wavelengths (310 and 350 nm) are the same, the differences in their decay rates clearly show that two different reaction intermediates are directly formed.

The spectral features in the case of 3- and 4-chloroanilines (Fig. 2a and 2b, respectively) at pH 6.6 are nearly the same as those observed in the case of the *ortho* isomer, differing only in detail. The spectrum with 4-chloroaniline has a distinct peak at 310 nm, unlike the shoulder observed for 3-chloroaniline. The absorption intensities at the two wavelengths are also different.

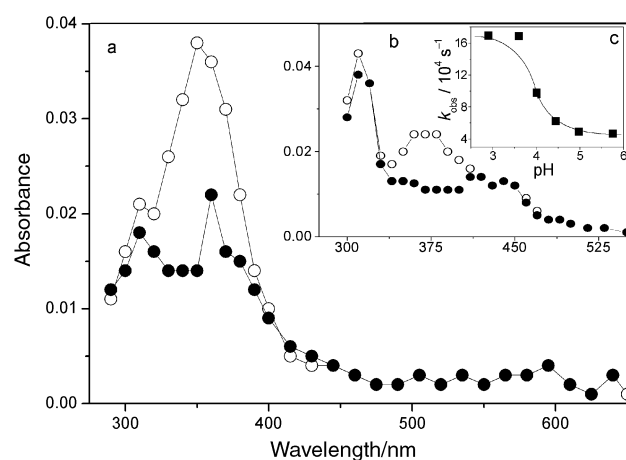


Fig. 2 Time-resolved transient absorption spectra at (○) 2 and (●) 40 μs after the pulse for the reaction of $\cdot\text{OH}$ with (a) 3- and (b) 4-chloroaniline. (c) The plot of rate of decay at 370 nm *versus* pH for the reaction of $\cdot\text{OH}$ with 4-chloroaniline.

For instance, the intensity at 350 nm is higher by 50% in the spectrum measured with 3-chloroaniline than that observed in 2- and 4-chloroanilines. However, the trend is reversed at the lower wavelength, where its intensity in the *para* isomer is doubled compared to that measured with the *meta* isomer. Similar to 2-chloroaniline, a first-order decay was also found at 350 nm in the case of the *meta* ($k \sim 5.6 \times 10^4 \text{ s}^{-1}$) and the *para* ($k \sim 6.5 \times 10^4 \text{ s}^{-1}$) isomers.

The absorption spectra in the $\cdot\text{OH}$ reaction with 4-chloroaniline were also recorded at pH 3.0, 4.6 and 9.0. The spectra measured at these pH values are nearly identical and were found to be similar to those measured in neutral solutions (pH = 6.6). Since the pK_a of 4-chloroaniline is 4.1, at pH 3 it exists in its protonated form (>90%) and the rate of the $\cdot\text{OH}$ reaction at this pH was estimated to be nearly five times slower than in neutral solutions, which can be explained on the basis of the decreased electron density due to the electron-withdrawing nature of the protonated amino group. The rate of decay of absorption at 370 nm was enhanced with increasing acidity. A plot of the rate of this decay (k_{obs}) *versus* pH has shown pK_a -type behaviour (Fig. 2c) and the pK_a of the resulting radical was estimated to be 3.9.

A comparison of the spectra reported² in the reaction of OH radical with aniline at 2 μs and 4-chloroaniline (0.5 μs) measured by us in acidic media shows that the former was composed of peaks at 350, 406 and 423 nm with negligible absorption at 310 nm. Moreover, the spectrum with aniline at 24 μs after the pulse showed significant decay of absorption at 350 nm with consequent increase in absorption at 406 and 423 nm. In contrast, the behaviour in the case of chloroanilines on a longer time scale did not reveal any significant spectral changes.

When Cl is replaced by the electron-donating OH group, the spectra obtained at 2 μs after the pulse with the *ortho* and *para* isomers are distinctly different from that measured with the *meta* isomer. Both 2- and 4-hydroxyanilines have a very high intense peak at 320 nm with a shoulder at 350 nm in the case of *ortho* and a relatively weak peak around 440 nm with the *para* isomer, whereas the spectrum with 3-hydroxyaniline has two peaks at 330 and 450 nm with nearly equal intensities. The transient absorption spectra recorded in 3- and 4-hydroxyanilines at pH 6.8 are shown in Fig. 3. No further significant changes were seen in the spectra recorded at 40 μs after the pulse at 320 nm and the usual bimolecular decay was only noticed on a longer time scale (2000 μs) as shown in the inset of Fig. 3.

Dichloroanilines. The general characteristics of the transient absorption spectra measured in the reaction of $\cdot\text{OH}$ with 2,4-, 2,5-, 2,6- and 3,4-dichloroanilines at neutral pH (\sim 6.8)

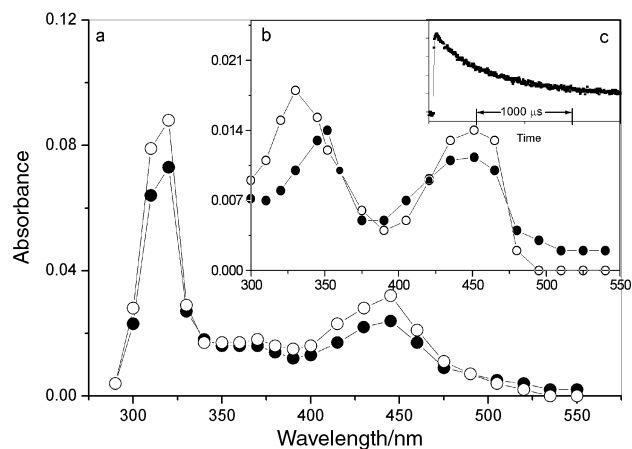


Fig. 3 Time-resolved transient absorption spectra in the reaction of $\cdot\text{OH}$ at (○) 2 and (●) 40 μs after the pulse with (a) 4- and (b) 3-hydroxyanilines. (c) Decay at 320 nm in the reaction of $\cdot\text{OH}$ with 4-hydroxyaniline.

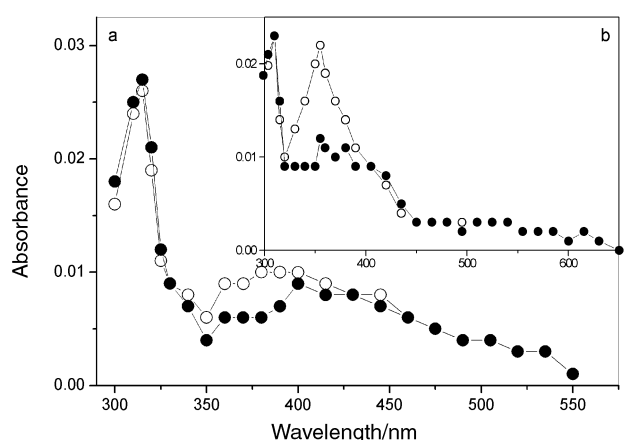


Fig. 4 Time-resolved transient absorption spectra at (○) 2 and (●) 40 μs after the pulse in the reaction of $\text{O}^{\cdot-}$ with (a) 4- and (b) 3-chloroanilines.

essentially remained identical to those obtained with monochloroanilines, though the spectral intensities are different.

(ii) Reactions of $\text{O}^{\cdot-}$. All the three spectra measured in the reaction of $\text{O}^{\cdot-}$ with the isomers of monochloroanilines at 2 μs after the pulse have a common peak at 310 nm. An additional distinct peak at 350 nm was seen only in the case of 3-chloroaniline; this decayed rapidly as can be seen from the spectra recorded at 20 μs shown in Fig. 4. The rate of this decay was found to follow first order kinetics with $k = 3.1 \times 10^4 \text{ s}^{-1}$. The fit of the data for the bimolecular decay was unsatisfactory. Moreover, the first half-life of the species decaying by second-order (dose rate = 1.5 Gy per pulse) assuming $k \sim 8 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ is estimated to be $>100 \mu\text{s}$ and therefore, the measured first-order rate constant is fairly accurate. Similarly to 3-chloroaniline, the spectra measured in the reaction of $\text{O}^{\cdot-}$ with 2,5-, 2,6- and 3,4-dichloroanilines have shown a sharp intense peak at 310–320 nm and an additional broad maximum around 360–380 nm.

(iii) Reaction of N_3^{\cdot} . The spectral behaviour in the reaction of N_3^{\cdot} with 2-, 3- and 4-chloroanilines in neutral solutions (pH = 6.5) is nearly the same with two peaks around 320 and 415 nm, the ratio of their intensities being 3 : 1. The intensities at the two wavelengths remained unchanged in the spectra recorded at 50 μs after the pulse. The spectrum obtained with 4-chloroaniline as an example is given in Fig. 5a. The spectrum recorded at pH 10 is almost identical to that measured in neutral solution. However, the spectrum recorded at 2 μs after

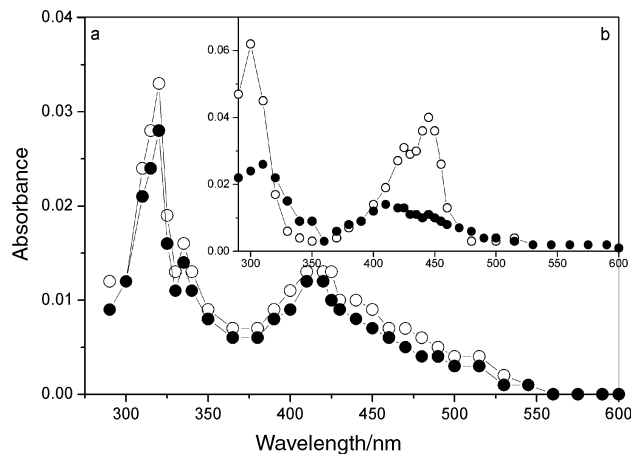


Fig. 5 Time-resolved transient absorption spectra at (○) 2 and (●) 40 μs after the pulse in the reaction of N_3^{\cdot} with 4-chloroaniline at (a) pH 6.5 and (b) pH 5.0.

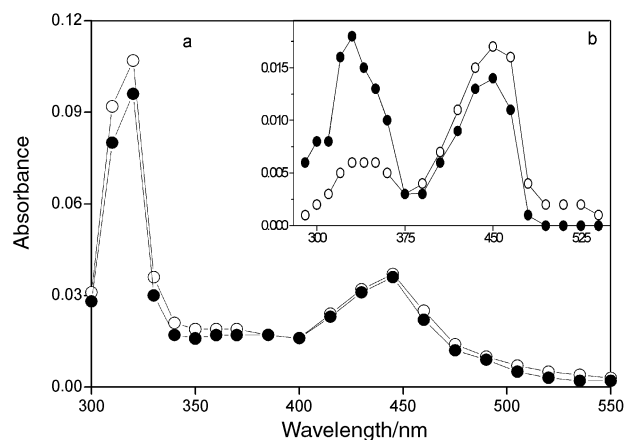


Fig. 6 Time-resolved transient spectra at (○) 2 and (●) 40 μs after the pulse in the reaction of N_3^{\cdot} with (a) 4- and (b) 3-hydroxyanilines.

the pulse in acidic medium (pH = 5.0) shows a very intense peak at 310 nm and relatively lower, but still significant, peaks at 410 and 440 nm. This spectrum, shown in Fig. 5b, quickly transforms into a spectrum similar to that observed in neutral solutions. Therefore, the spectrum with peaks at 320 and 415 nm is attributed to the anilino radical.² The formation of an anilino radical due to the reaction of the $\cdot\text{OH}$ radical with aniline has already been reported.^{25,26}

A nearly identical spectrum, as in the case of 4-chloroaniline ($\lambda_{\text{max}} = 310$ and 415 nm), was observed in the reaction of N_3^{\cdot} with 4-hydroxyaniline after the completion of the reaction (2 μs). In contrast, not only are all the features of the spectrum obtained in the reaction of N_3^{\cdot} with 3-hydroxyaniline different from the *para* isomer, even the rate of its reaction was lowered by an order of magnitude. The spectra recorded after the completion of the reaction in 3-hydroxyaniline (40 μs) and 4-hydroxyaniline (2 μs) are given in Fig. 6. The spectra recorded for the reaction of N_3^{\cdot} with 2,4-, 2,5- and 3,4-dichloroanilines are almost identical with those obtained for monochloroanilines.

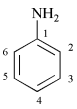




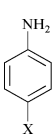
(c) Semi-empirical quantum chemical calculations

Semi-empirical PM3²⁷ quantum chemical calculations were carried out using the program GAMESS.²⁸ The residual atomic charges from the Mulliken population analysis for the optimized structures of substituted anilines studied herein are displayed in Table 2. The charge distribution for the carbon centers of the chloro- and hydroxy-aniline isomers has been given along with those for aniline, phenol and chlorobenzene. As may be readily seen, the activation of the *ortho* and *para*

Table 2 Electronic charge distribution at different carbons in aniline, chlorobenzene, dichloroanilines and hydroxyanilines

	1	2	3	4	5	6
Aniline	-0.02	-0.28	-0.13	-0.26	-0.13	-0.28
Phenol	0.09	-0.24	-0.15	-0.24	-0.14	-0.29
Chlorobenzene	-0.13	-0.19	-0.18	-0.19	-0.18	-0.19
2-Chloroaniline	-0.08	-0.18	-0.16	-0.22	-0.16	-0.23
3-Chloroaniline	-0.07	-0.25	-0.09	-0.23	-0.14	-0.24
4-Chloroaniline	-0.08	-0.23	-0.16	-0.16	-0.16	-0.23
2,3-Dichloroaniline	-0.06	-0.19	-0.10	-0.22	-0.14	-0.23
3,4-Dichloroaniline	-0.07	-0.24	-0.10	-0.18	-0.14	-0.23
2,4-Dichloroaniline	-0.08	-0.17	-0.16	-0.16	-0.16	-0.22
3,5-Dichloroaniline	-0.05	-0.25	-0.08	-0.24	-0.08	-0.25
2,5-Dichloroaniline	-0.06	-0.19	-0.14	-0.22	-0.09	-0.24
2,6-Dichloroaniline	-0.07	-0.18	-0.16	-0.21	-0.16	-0.18
2-Hydroxyaniline	-0.23	0.13	-0.25	-0.15	-0.23	-0.17
3-Hydroxyaniline	-0.04	-0.30	0.13	-0.33	-0.11	-0.28
4-Hydroxyaniline	-0.12	-0.19	-0.21	0.06	-0.26	-0.19

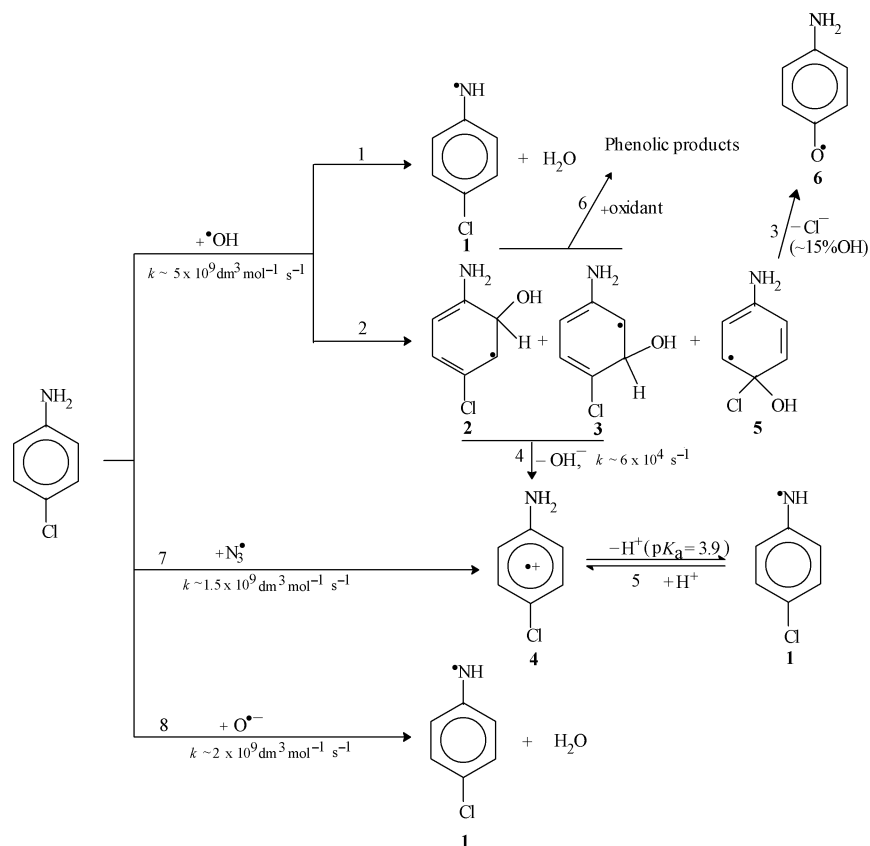
Table 3 The heats of formation (kJ mol^{-1}) of isomeric OH adducts of chloro- and hydroxy-anilines using the PM3 method

	1	2	3	4	5	6
	-22.6	-50.6	-33.9	42.3	-33.9	-50.6
	-65.3	-57.8	-52.7	-65.7	-52.7	-57.7
	-223.4	-221.3	-213.4	-228.0	-213.4	-221.3
 X = Cl X = OH	-45.2 -218.4	-84.5 -247.3	-84.5 -213.4	-70.3 -221.0	-73.2 -230.1	-80.3 -228.9
 X = Cl X = OH	-42.7 -207.6	-80.8 -241.0	-74.5 -232.6	-71.6 -230.5	-61.9 -220.1	-84.5 -243.5
 X = Cl X = OH	-47.3 -210.9	-72.8 -232.2	-66.9 -230.1	-79.1 -243.9	-66.9 -230.1	-72.8 -232.2

positions is more pronounced in the case of aniline and phenol than in chlorobenzene. On the other hand, the deactivation of the carbon bonded to the hydroxy group is greater in 2- and 3-hydroxyanilines. The deactivation of the *ipso* carbon (bonded to NH_2) of the chloroaniline isomers has been nearly the same. Also the +I and +R effects of NH_2 and OH groups, respectively, make the carbon bonded to the NH_2 group electron rich for 2-hydroxyaniline; the residual charge on this carbon is nearly twice as large as in 4-hydroxyaniline and, further, about six times larger than in the *meta* isomer. PM3 calculations predict the *meta* positions in substituted anilines to be electron rich with the exception of 3-hydroxyaniline. The finer distinction for the preference of *ortho* and *para* positions for the electrophile could not, however, be made. It may, however, be inferred that the $\cdot\text{OH}$ attack extends over more than two carbon positions in these systems.

In Table 3, we report the PM3 heats of formation (ΔH_f) of the isomeric OH adducts of chloro- and hydroxy-anilines for the equilibrium geometries, along with those for aniline, chlorobenzene and phenol. The ΔH_f values for these OH adducts of $\text{C}_6\text{H}_5\text{NH}_2$, $\text{C}_6\text{H}_5\text{Cl}$ and $\text{C}_6\text{H}_5\text{OH}$ formed from the attack at the *ortho* and *para* positions are greater (12–16 kJ mol^{-1}) than the

corresponding ones formed by the addition to the *meta* carbon. The heats of formation of the OH adducts of chloroanilines formed from $\cdot\text{OH}$ attack at the NH_2 bonded carbon (*ca.* -45 kJ mol^{-1}) are larger than those estimated for other isomers (*ca.* -75 kJ mol^{-1}) of chloroanilines. Hence, the attack at the carbon bonded to the amino group is less favourable in chloroanilines. In 2- and 4-hydroxyanilines the attack at the carbon bonded to the hydroxy group will be preferred over other sites. The ΔH_f values for the adducts turn out to be -247.3 and -243.9 kJ mol^{-1} for 2- and 4-hydroxyanilines, respectively. In the case of 3-hydroxyaniline, however, the attack is favoured at the *ortho* position with respect to the amino group. Thus, the $\cdot\text{OH}$ attack in hydroxyanilines may be favoured relative to chloroanilines, since the intermediate adducts are stabilised more. The observed transient absorption spectra, on the other hand, reveal that the OH adducts of chloroanilines are stable at least up to 2 μs following the pulse, in contrast to the behaviour observed with hydroxyanilines, wherein the formation of only anilino radicals was seen on the same time scale. Therefore, it may be conjectured that the ensuing anilino radicals formed from the dehydration of OH adducts of hydroxyanilines are more stabilised. The theoretical calculations do not support



Scheme 1 $\cdot\text{OH}$, $\text{N}_3\cdot$ and $\text{O}^{\cdot-}$ reaction mechanism with 4-chloroaniline.

these observations. In addition to the heats of formation of these intermediates the solvation and other environmental factors^{29–31} contribute greatly in deciding the reactivity.

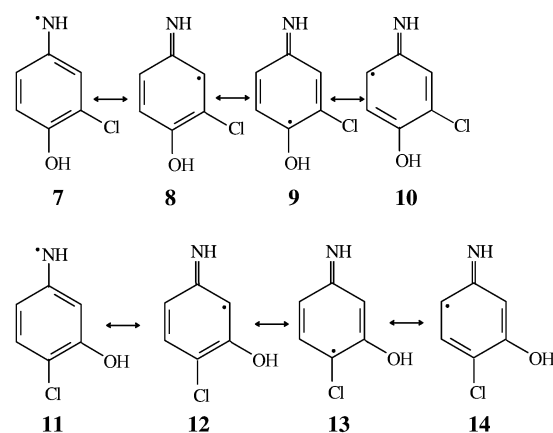
(d) Reaction mechanism

The $\cdot\text{OH}$ reaction mechanism with isomers of chloroanilines involves addition as well as direct H abstraction. In agreement with earlier work,² the intermediates having absorption maxima around 350–380 nm are assigned to the OH adducts and those absorbing at 310–320 nm to the anilino radicals. These two reactions are depicted, considering 4-chloroaniline as an example, because the $\cdot\text{OH}$ attack at the two positions (C-2/C-6 and C-3/C-5) (reactions 1 and 2, Scheme 1) is predominant. The heats of formation and the charge distribution data indicate at possibility of the formation of *ipso* complexes from $\cdot\text{OH}$ attack at carbon bonded to NH_2 . Thus, three $\cdot\text{OH}$ adducts are formed as a result of the direct addition of the $\cdot\text{OH}$ radical as shown in Scheme 1. The formation of the *ipso* complex from the $\cdot\text{OH}$ attack at the carbon bonded to NH_2 is ruled out based on the charge distribution and heats of formation data. Similarly, the attack at the Cl-substituted carbon (reaction 3, Scheme 1) is not significant due to steric hindrance. This was confirmed by the estimation of free Cl^- ions by HPIC (DIONEX 500, column = AS 11, eluent = $2 \times 10^{-3} \text{ mol dm}^{-3} \text{ NaOH}$) formed on gamma irradiation of 2-, 3- and 4-chloroanilines (dose $\sim 300 \text{ Gy}$). For example, the amount of Cl^- ions was estimated to be $\sim 15\%$ OH considering $G(\cdot\text{OH}) = 5.6$ and was found to be independent of the position of Cl.

In addition to direct H abstraction, the time-resolved spectral studies have shown the formation of anilino radical by elimination of OH^- (reaction 4, Scheme 1) followed by deprotonation (reaction 5) from the initially-formed OH adducts. The extent of the two reactions, *i.e.* $\cdot\text{OH}$ addition to the ring and direct H abstraction, is determined by the positions of the NH_2 and Cl groups. On the basis of the activation effects of the NH_2 and Cl groups in 4-chloroaniline (Tables 2 and 3), the yields of

the OH adducts **2** and **3** are expected to be nearly equal. It is, however, likely that radical **2** is involved, as it is more readily oxidised than radical **3** (reaction 6) because of the *ortho*- and *para*-directing nature of the NH_2 group facilitating the electron transfer.

The competing H abstraction from the NH_2 group (reaction 1, Scheme 1) gains significance in systems where the anilino radicals are stabilised. The anilino radicals are stabilised in *ortho* and *para* isomers of chloroanilines. The mesomeric structures are shown in Scheme 2 in the case of 3-chloroaniline and 4-chloroaniline.



Scheme 2 Different mesomeric structures of anilino radicals formed from $\cdot\text{OH}$ reaction with 3- and 4-chloroanilines.

The anilino radical is more stabilised due to structure **9**, where the electron deficient carbon is attached directly to the electron-rich OH group. Such stabilisation is not possible in the case of the *meta* isomer. Moreover, radical **7** is also better stabilised than radical **11**, where the electron deficient NH group is at a position *para* to the OH group. This must be the reason for the

observed differences in the spectral intensities at 310–320 nm among the three isomers. The observed order for the extent of the direct H abstraction is *para* > *ortho* > *meta*, assuming that the molar extinction coefficients of the anilino radicals of the three isomers are nearly identical. In contrast, the OH⁻ elimination reaction from the OH adducts seems to be predominant in the case of 3-chloroaniline (inset of Fig. 4). This is because the positive charge of the radical cation formed from the OH⁻ elimination is centered at carbons activated by both NH₂ and Cl groups; such an additive effect is not possible in the other two isomers.

In contrast to chloroanilines, the deprotonation of the radical cation may either occur at the amino group to give the anilino radical or at the phenolic group to give a phenoxyl radical. In order to ascertain this aspect, the transient absorption spectra for the reaction of [•]OH and N₃[•] radicals with 4-methoxyaniline were measured, as the one-electron oxidation by the N₃[•] radical leads to the formation of anilino radical following deprotonation of the radical cation. Both the spectra have two very broad peaks ($\lambda_{\text{max}} = 320$ and 440 nm) with nearly equal intensities. Though the absorption maxima of the spectra obtained in the reaction of OH radical with the two systems (4-hydroxy- and 4-methoxy-anilines) are nearly identical, their nature and intensity ratios are different. The peak at 310 nm in the spectrum with 4-hydroxyaniline is sharp and is 2.5 times more intense as compared to the peak at 440 nm. Therefore, we are tempted to attribute this spectrum to the phenoxyl radical rather than the anilino radical.

The main pathway in the nucleophilic O^{•-} reaction is exclusively considered to be by H abstraction (reaction 8, Scheme 1) in the case of *ortho* and *para* isomers, while addition also takes place in the *meta* isomer. This is because of the stabilisation of the anilino radicals of the *ortho* and *para* isomers as explained before (Scheme 2).

The spectra obtained in the N₃[•] reaction with the three isomers of chloroanilines in neutral solutions appear to be solely due to the anilino radical (reaction 7) and the molar extinction coefficients estimated from the spectral data [$G(\text{N}_3^{\bullet}) = 5.6$] are about 2450 (310 nm) and 1100–1200 dm³ mol⁻¹ cm⁻¹ (420 nm) in the case of 2- and 3-chloroanilines. These values are higher in the case of the *para* isomer (3180 and 1450 dm³ mol⁻¹ cm⁻¹). It is interesting to note that the initially-formed radical cation in monochloro- and hydroxy-anilines is not stabilised even at pH = 5.0, unlike the case of aniline. This is due to the fact that the pK_a of the radical cation is lower than 5. Thus the stabilisation of the anilino radicals by the substituents and the deprotonation of the radical cation, therefore, appears to be an effective process.

Conclusions

[•]OH, O^{•-} and N₃[•] react with chloro- and hydroxy-derivatives of aniline at diffusion-controlled rates with $k > 10^9$ dm³ mol⁻¹ s⁻¹ and the rates are nearly identical for all isomers of chloroanilines. The transient absorption spectra in the [•]OH reaction with mono- and di-chloroanilines have absorption maxima at 310–320 and 350–380 nm, which are assigned to the anilino and OH adduct radicals. The OH radical reaction mechanism involves both addition and direct H abstraction and the extent of the two reactions is determined by the position of the substituents. The initially-formed OH adduct then undergoes dehydration followed by deprotonation to give the anilino radical. The attack of the OH radical at the carbon bonded to Cl is a minor pathway (not more than 15% OH) as was confirmed by the detection of the free Cl⁻ ions. In the case of hydroxyanilines, the formation of phenoxyl radical is favoured to the anilino radical. The charge distribution and heats of formation data evaluated from the semi-empirical quantum calculations are in accord with the activation and deactivation effects of the substituents.

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