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Radiation-induced oxidation of substituted benzaldehydes: a pulse radiolysis study[†]

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ABSTRACT: The reactions of the oxidizing radicals hydroxyl radical ($^{\cdot}$OH), azidyl radical ($N_3^{\cdot}$) and sulfate radical anion ($SO_4^{\cdot-}$) with hydroxy-, methoxy-, chloro- and nitro-substituted benzaldehydes were studied by pulse radiolysis. The rate constants for the $^{\cdot}$OH reaction [$k \approx (2.6–12.0) \times 10^9\,l\,mol^{-1}\,s^{-1}$] with these compounds are higher than those for the $N_3^{\cdot}$ or $SO_4^{\cdot-}$ reactions [$k \approx (0.01–4.2) \times 10^9\,l\,mol^{-1}\,s^{-1}$]. The $^{\cdot}$OH reaction shows a significant substituent effect which is reflected in the rate constants ($k \approx 12.0 \times 10^9\,dm^3\,mol^{-1}\,s^{-1}$ with hydroxybenzaldehyde and $k \approx 3.0 \times 10^9\,dm^3\,mol^{-1}\,s^{-1}$ with nitrobenzaldehyde). The transient species produced by the reaction of $^{\cdot}$OH with the *m*-substituted benzaldehydes shows an absorption maximum at 370–400 nm, whereas the *p*-substituted isomers exhibit two absorption peaks centred around 325 and 410 nm, except in the case of *p*-nitrobenzaldehyde, which shows only a single peak at 330 nm. These spectra are identical with the spectra obtained for the $N_3^{\cdot}$ or $SO_4^{\cdot-}$ reactions with substituted benzaldehydes. $^{\cdot}$OH adduct formation and subsequent decomposition to the corresponding phenoxyl radicals is the main reaction channel for the $^{\cdot}$OH-induced oxidation of substituted benzaldehydes. One-electron oxidation by $N_3^{\cdot}$ or $SO_4^{\cdot-}$ of substituted benzaldehydes proceeds via an electron transfer process producing the corresponding radical cations. Copyright © 2004 John Wiley & Sons, Ltd.

KEYWORDS: benzaldehydes; radiation-induced oxidation; radicals; pulse radiolysis

INTRODUCTION

The pulse radiolysis technique is most widely used tool for evaluating the kinetics and determining the spectral nature of the transient species involved in a reaction from optical absorption and conductance detection measurements. These data combined with product analysis[1–5] using HPLC, HPIC and GC–MS techniques under steady-state conditions have made radiation chemical methods particularly unique.

The weakly electrophilic $^{\cdot}$OH radical ($\rho^+ = -0.5$)[6,7] is known to react with substituted benzenes by addition,[8–16] forming the corresponding hydroxycyclohexadienyl radical. The rate constants for $^{\cdot}$OH reactions with benzene derivatives are dependent on the substituent. Our earlier work[17–24] on several substituted benzenes of the type $C_6H_{5-n}X_nY$ (where X = H, halogen or OH and Y = H, halogen, NH_2, CHO, $COCH_3$, COC_6H_5, CH_3, CH_2Cl, $CHCl_2$ or CF_3) has provided valuable information on the stucture–reactivity relationship leading to the proposal of the mechanistic pathways involved in the free radical-induced degradation of these compounds. However, the study of the oxidation/reduction of substituted benzaldehydes has been limited.[8,25] Our recent investigation[25] on the oxidation of *o*-, *m*- and *p*-hydroxybenzaldehydes and acetophenone by $^{\cdot}$OH and $N_3^{\cdot}$ indicated addition and electron transfer processes, respectively, and different transient absorption spectra for the $^{\cdot}$OH adducts of *m*- and *p*-hydroxybenzaldehydes were reported. Therefore, it was of interest to extend the investigation to other substituted benzaldehydes, especially with electron-donating or electron-withdrawing group(s), to gain further insights into the structure–reactivity correlation. In this paper, we report the reactions of $^{\cdot}$OH, $N_3^{\cdot}$ and $SO_4^{\cdot-}$ with benzaldehydes containing OH, OCH_3, Cl or NO_2 substituents.

EXPERIMENTAL

Substituted benzaldehydes were obtained from Fluka or Sisco ($\geq$98%). The compounds (*m*- and *p*-methoxybenzaldehyde and *m*-chlorobenzaldehyde) were distilled prior to their use. Solutions were freshly prepared using water purified with a Millipore Milli-Q system. High-purity N_2O and N_2 gases were used for saturating the solutions before dissolution of the substrate to prevent volatilization. All the experiments were carried out at room temperature ($\sim$27 °C).

Pulse radiolysis experiments were carried out using a 7 MeV linear accelerator, which generates single electron

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pulses of 50 ns duration. The transient absorption spectra were recorded on a digital oscilloscope interfaced to a computer for data analysis. The details of the pulse radiolysis set-up and data handlings have been described elsewhere.[25,26] Doses/pulses were determined by using aerated aqueous solutions containing 10^{-2} mol dm^{-3} KSCN and taking $G\epsilon_{500} = 21\,522$ mol^{-1} dm^3 cm^{-1} for the transient[27,28] $(SCN)_2^{-\cdot}$. The doses/pulses used for these experiments were in the range 12–15 Gy.

Radiolysis of water leads to the generation of primary radiolytic products:

$$H_2O \rightsquigarrow {}^{\cdot}OH, H^{\cdot}, e^-_{aq}, H_2O_2, H_2, H_3O^+ \qquad (1)$$

The radiation-chemical yields (G values) of the primary radicals are $G({}^{\cdot}OH) \approx G(e^-_{aq})$ (2.8×10^{-7} mol J^{-1} and $G(H^{\cdot}) = 0.55 \times 10^{-7}$ mol J^{-1}.

e^-_{aq} may be quantitatively converted into $^{\cdot}OH$ by saturating the aqueous solution with N_2O:

$$e^-_{aq} + N_2O \xrightarrow{H_2O} N_2 + OH^- + {}^{\cdot}OH \qquad (2)$$

where $k = 9.1 \times 10^9$ mol^{-1} dm^3 s^{-1}.

$N_3^{\cdot}$ was generated in N_2O-saturated aqueous solution containing 2×10^{-2} mol dm^{-3} NaN_3, where the $^{\cdot}OH$ is converted into $N_3^{\cdot}$:

$$N_3^- + {}^{\cdot}OH \rightarrow N_3^{\cdot} + OH^- \qquad (3)$$

where $k = 1.2 \times 10^{10}$ mol^{-1}dm^3 s^{-1}.

$SO_4^{-\cdot}$ was produced by the reaction of e^-_{aq} and $H^{\cdot}$ in an N_2-saturated solution containing 1.5×10^{-2} mol dm^{-3} $K_2S_2O_8$ and 2×10^{-4} mol dm^{-3} *tert*-butyl alcohol:

$$S_2O_8^{2-} + e^-_{aq} \rightarrow SO_4^{-\cdot} + SO_4^- \qquad (4)$$

$k(e^-_{aq}) = 1.2 \times 10^{10}$ mol^{-1} dm^3 s^{-1}.

RESULTS AND DISCUSSION

Transient absorption spectra for $^{\cdot}OH$, $N_3^{\cdot}$ and $SO_4^{-\cdot}$ reactions

The time-resolved transient absorption spectra determined for the reactions of $^{\cdot}OH$ with *m*- and *p*-methoxybenzaldehydes are shown in Figs 1 and 2, respectively. The spectrum for the *m*-methoxybenzaldehyde shows a single peak at 400 nm (Fig. 1) whereas an additional peak at shorter wavelength (325 nm) was observed for the *p*-isomer (Fig. 2). The time-resolved spectral measurements revealed a first-order decay of the transient (400–410 nm) with $k = 7.2 \times 10^4$ and 1.7×10^5 s^{-1} for *m*- and *p*-methoxybenzaldehydes, respectively. These spectra are identical with those

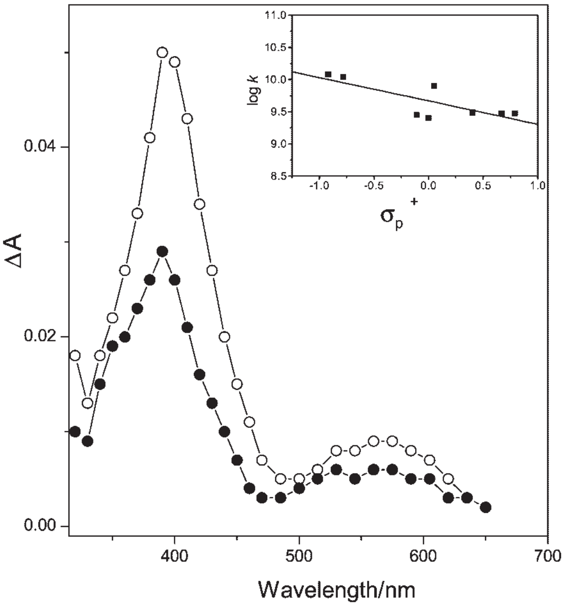


Figure 1. Time-resolved transient absorption spectrum obtained for the reaction of $^{\cdot}OH$ with *m*-methoxybenzaldehyde (1×10^3 mol dm^{-3}), 2 (○) and 15 μs (●) after the pulse. Inset: Hammett plot for the reaction of $^{\cdot}OH$ with substituted benzaldehydes. Dose/pulse = 1.5 krad

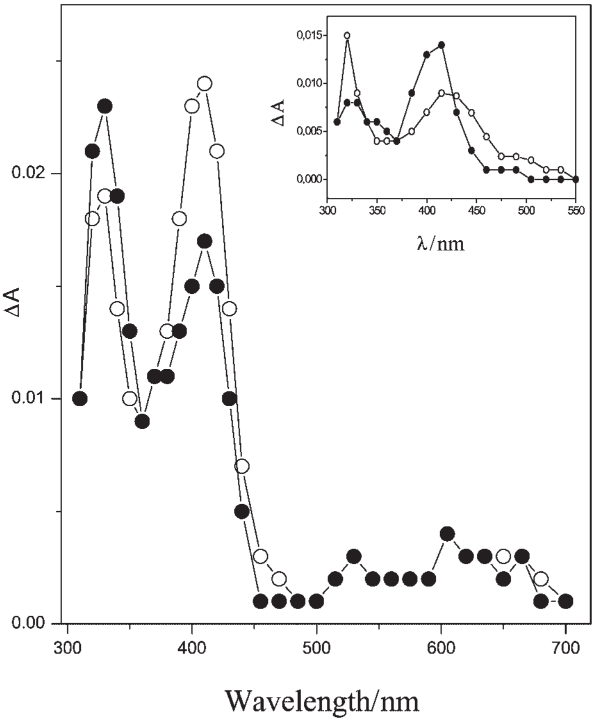


Figure 2. Time-resolved transient absorption spectrum obtained for the reaction of $^{\cdot}OH$ with *p*-methoxybenzaldehyde (1×10^3 mol dm^{-3}), 2 (○) and 15 μs (●) after the pulse. Inset: time-resolved transient absorption spectrum recorded in the reaction of the $SO_4^{-\cdot}$ radical with *p*-methoxybenzaldehyde (1×10^3 mol dm^{-3}), 2 (○) and 40 μs (●) after the pulse. Dose/pulse = 1.5 krad

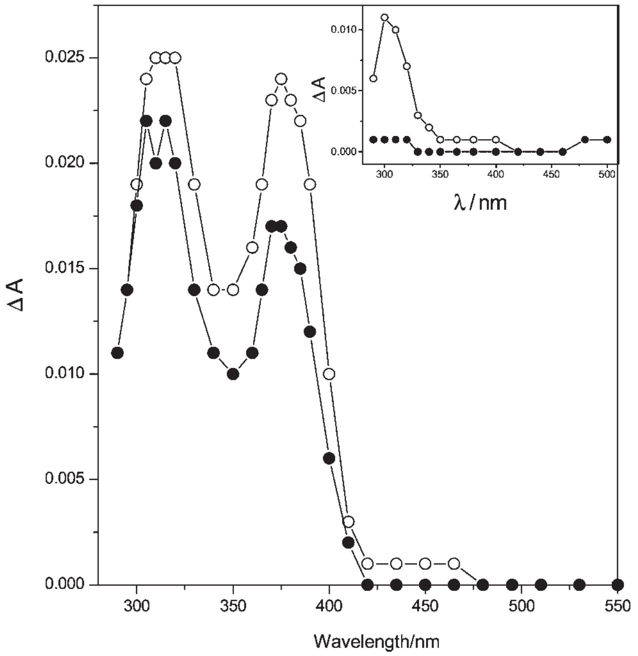


Figure 3. Time-resolved transient absorption spectra recorded for the reaction of ˙OH, 2 (○) and 15 μs (●), and (inset) N$_3^{\cdot}$, 2 (O) and 40 μs (●) after the pulse, with *p*-chlorobenzaldehyde (1 × 10^3 mol dm^{-3}). Dose/pulse = 1.5 krad

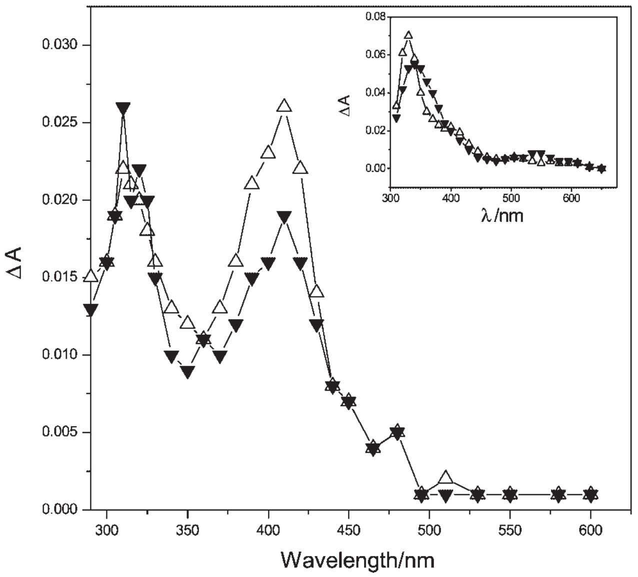


Figure 4. Time-resolved transient absorption spectra obtained for the reaction of ˙OH with *m*-nitrobenzaldehyde and (inset) *p*-nitrobenzaldehyde, 2 (Δ) and 15 μs (▼) after the pulse (1 × 10^3 mol dm^{-3}). Dose/pulse = 1.5 krad

determined for the reaction of ˙OH with the corresponding isomers of hydroxybenzaldehydes[25] but the first-order rate of decay was slightly higher ($k = 4.6 \times 10^5$ s^{-1} for *m*-hydroxybenzaldehyde and 5.5×10^5 s^{-1} for *p*-hydroxybenzaldehyde). The absorption spectrum recorded for the reaction of ˙OH with *m*-chlorobenzaldehyde exhibits a single peak around 370 nm. In contrast, the spectrum observed with the *p*-isomer shows two maxima at 310 and 375 nm (Fig. 3), which is similar to that observed in the case of *p*-methoxybenzaldehyde. In the reaction of ˙OH with *m*-nitrobenzaldehyde, two maxima were observed at 315 and 410 nm (Fig. 4), whereas a single peak at 340 nm was observed with *p*-nitrobenzaldehyde (inset). Furthermore, a delayed first-order increase ($k = 4.4 \times 10^4$ s^{-1}) in absorption at 360 nm was recorded in the latter case. The transient spectra for the ˙OH reaction with *m*-isomers with an electron-donating group (OCH_3 or Cl) also showed a single peak whereas the spectra for the *p*-isomers have two peaks. The trend is reversed with the systems containing electron-withdrawing groups (e.g. nitrobenzaldehyde). These spectra are assigned to the ˙OH adduct, which subsequently undergoes elimination to form the phenoxyl radical.

The spectral intensities measured in the reaction of the N$_3^{\cdot}$ with *p*-methoxy-and *p*-chlorobenzaldehyde was found to be low. In the case of *p*-methoxybenzaldehyde, the spectrum exhibited two peaks at 325 and 400 nm, which is similar to that observed for the ˙OH reaction. However, in the case of *p*-chlorobenzaldehyde, the time-resolved spectrum exhibited a single peak at 300 nm, which decayed almost completely within 40 μs (Fig. 3, inset). A similar spectrum was obtained for the reaction of N$_3^{\cdot}$ with *p*-nitrobenzaldehyde. The time-resolved spectrum for the reaction of SO$_4^{\cdot-}$ with *p*-methoxybenzaldehyde is identical with the corresponding spectrum for the ˙OH reaction (Fig. 2, inset). Similarly, the spectra of all the isomers (*m*- and *p*-methoxy-, *m*- and *p*-chloro- and *m*- and *p*-nitrobenzaldehydes) are similar to the corresponding spectra measured for the ˙OH reaction, indicating the involvement of the same transient species. Therefore, the transient species involved in the reaction of N$_3^{\cdot}$ or SO$_4^{\cdot-}$ with substituted benzaldehydes is assigned to the phenoxyl radical. Since the yield (*G*) of SO$_4^{\cdot-}$ [$G(SO_4^{\cdot-}) = 3.3 \times 10^{-7}$ mol J^{-1}] is lower than that of the ˙OH [$G(^{\cdot}OH) = 5.6 \times 10^{-7}$ mol J^{-1}], the intensities of the spectra for the SO$_4^{\cdot-}$ reaction are lower.

Kinetics and mechanisms

Kinetics of reactions of ˙OH, N$_3^{\cdot}$ and SO$_4^{\cdot-}$. The rates for the reactions of ˙OH, N$_3^{\cdot}$ and SO$_4^{\cdot-}$ with substituted benzaldehydes were determined from the growth of the transient band at the respective λ_{max} in the solute concentration range (0.2–1) × 10^{-3} mol dm^{-3}. The second-order rate constants were evaluated from the slopes of the plots of k_{obs} versus [solute] and are given in Table 1 together with the absorption maxima (λ_{max}) of the transient intermediate. Also shown in Table 1 are the values reported[18,19,29] for selected substituted benzenes. As can be seen, the second-order rate constant for the reaction of ˙OH with *p*-methoxybenzaldehyde ($k = 11.0 \times 10^9$ mol^{-1} dm^3 s^{-1}) is higher by nearly an order of

Table 1. Second-order rate constants (k /10^9 mol^{-1} dm^3 s^{-1}) and absorption maxima (λ_{max}/nm) obtained for the reaction of $^{\cdot}$OH and $\mathrm{N}_3^{\cdot}$ with *m*- and *p*-substituted benzaldehydes

	$^{\cdot}$OH		$\mathrm{N}_3^{\cdot}$		$\mathrm{SO}_4^{-\cdot}$	
Compound	λ_{max}	k	λ_{max}	k	λ_{max}	k
Benzaldehyde	370	2.6	nd[a]	nd	370	0.7
m-Hydroxybenzaldehyde	400	7.7	370	(6.0)	410	4.2
p-Hydroxybenzaldehyde	325, 410	12.1	345	(11.6)	400	(5.9)
m-Methoxybenzaldehyde	400	8.0	nd	<0.01	400	0.43
p-Methoxybenzaldehyde	325, 410	11.0	325, 400	(0.13)	325, 410	0.8
m-Chlorobenzaldehyde	370	3.1	nd	<0.01	375	nd
p-Chlorobenzaldehyde	310, 375	2.8	300	13.0	310, 375	(2.7)
m-Nitrobenzaldehyde	315, 410	3.0	nd	<0.01	300, 410	nd
p-Nitrobenzaldehyde	330	3.0	360	<0.01	350	(0.45)
m-Cresol[b]	325	10.0	nd	nd	290, 390	3.8
p-Cresol[b]	305	9.2	nd	nd	290, 390	6.1
m-Chloroaniline[b]	310, 350	4.5	305, 410	2.0	nd	nd
p-Chloroaniline[b]	315, 370	5.0	315, 420	1.5	nd	nd
m-Chlorotoluene[b]	330	3.5	nd	nd	325	0.9
p-Chlorotoluene[b]	310	5.5	nd	nd	270, 315	1.1

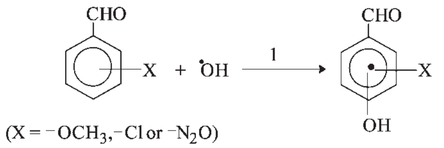
[a] nd, Not determined.
[b] The values for cresols, chloroanilines and chlorotoluenes are taken from Refs 18, 19 and 29.

magnitude than that of the *m*-isomer ($k = 8.0 \times 10^9$ mol^{-1} dm^3 s^{-1}). These rate constants are comparable to those measured for the reaction of $^{\cdot}$OH with *p*- and *m*-hydroxybenzaldehydes,[25] suggesting that OH and $\mathrm{OCH_3}$ groups activate the ring nearly to the same extent. This is in agreement with the reported[30] σ_p^+ value for the OH and $\mathrm{OCH_3}$ groups of -0.92 and -0.78, respectively. The second-order rate constant for the reaction of $^{\cdot}$OH with *m*-chlorobenzaldehyde ($k = 3.1 \times 10^9$ dm^3 mol^{-1} s^{-1}) is identical with that for the *p*-isomer ($k = 2.8 \times 10^9$ dm^3 mol^{-1} s^{-1}) and lower by an order of magnitude than those for the hydroxy- and methoxybenzaldehydes. When the Cl is replaced by $\mathrm{NO_2}$, the rate constants for the $^{\cdot}$OH reaction remains unaffected ($k = 3 \times 10^9$ dm^3 mol^{-1} s^{-1}) for both *m*- and *p*-nitrobenzaldehydes. The low rate constants for the reaction of $^{\cdot}$OH with *m*- and *p*-nitrobenzaldehydes could be due to the deactivation of the ring by the electron-withdrawing $\mathrm{NO_2}$ group.

A comparison of the rate constants for the $^{\cdot}$OH reaction obtained in the present study with those which we measured earlier[18,29] in related systems (*m*- and *p*-isomers of chloroaniline and chlorotoluene) shows that the rate constants are nearly diffusion controlled ($k \approx 3 \times 10^9$–1.2×10^{10} dm^3 mol^{-1} s^{-1}). In order to quantify the substituent effect in substituted benzaldehydes, the Hammett equation was employed and the plot of the dependence of the rate constants for the $^{\cdot}$OH reaction with the substituted benzaldehydes on σ_p^+ gives a good linear correlation of $\rho^+ = -0.4 \pm 0.09$ (Fig. 1, inset). This is in agreement with the reported values obtained by us[24] and by others earlier[6,7] (-0.4 to -0.52) for substituted benzenes, suggesting an addition reaction.

In the reaction of $\mathrm{N}_3^{\cdot}$ with *p*-hydroxybenzaldehyde, the second-order rate constant for the formation of the transient species at 350 nm was estimated as 1.16×10^{10} mol^{-1}dm^3 s^{-1}. In contrast, the rate was halved for the reaction of $\mathrm{N}_3^{\cdot}$ with the *m*-isomer ($k = 6 \times 10^9$ mol^{-1}dm^3 s^{-1}). The lowering of the rates is more pronounced for methoxybenzaldehydes, where a two orders of magnitude decrease in the rate constant was observed with the *p*-isomer ($k = 0.13 \times 10^9$ dm^3 mol^{-1} s^{-1}) relative to the hydroxybenzaldehydes. *m*-Methoxy- and *m*- and *p*-nitrobenzaldehydes (1×10^{-3} mol dm^{-3}) were found to be unreactive ($k \leq 1 \times 10^7$ dm^3 mol^{-1} s^{-1}) even at 50 μs, as used in our investigation. Surprisingly, a very high second-order rate constant was observed for the reaction of $\mathrm{N}_3^{\cdot}$ with *p*-chlorobenzaldehyde ($k = 1.3 \times 10^{10}$ dm^3 mol^{-1} s^{-1}). This can be explained by the fact that the activation of the *m*-position by the CHO group in the *m*-isomers of methoxy and chlorobenzaldehydes is deactivated by the electron-donating $\mathrm{OCH_3}$ or Cl groups. The lack of reactivity in the *m*- and *p*-nitrobenzaldehydes is attributed to the electron-withdrawing nature of $\mathrm{NO_2}$ and CHO groups. Furthermore, the reduction potential of these compounds must be higher than that of $\mathrm{N}_3^{\cdot}/\mathrm{N}_3^-$ ($E^\circ = 1.33$ V). When the more powerful one-electron oxidant $\mathrm{SO}_4^{-\cdot}$ ($E^\circ = 2.5$–3.1 V) was used, all the derivatives were found to react with $\mathrm{SO}_4^{-\cdot}$ under identical conditions. The transient absorption spectra observed in the reaction of $\mathrm{SO}_4^{-\cdot}$ with these substituted benzaldehydes were fully developed within 2 μs, indicating that the rates are nearly diffusion controlled [$k \geq (0.7$–$6.0) \times 10^9$ dm^3 mol^{-1} s^{-1}].

Mechanisms of reactions of $^{\cdot}$OH, $\mathrm{N}_3^{\cdot}$ and $\mathrm{SO}_4^{-\cdot}$. $^{\cdot}$OH generally reacts by addition or H abstraction or both. Considering the rate constants for the reaction of $^{\cdot}$OH with the methoxy-, chloro- and nitrobenzaldehydes [$k = (2.6$–$12.1) \times 10^9$ dm^3 mol^{-1} s^{-1}], direct H abstraction, the rate of which is expected to be lower than that of addition by one to two orders of magnitude, is considered unlikely. Therefore, it is proposed that the



Scheme 1

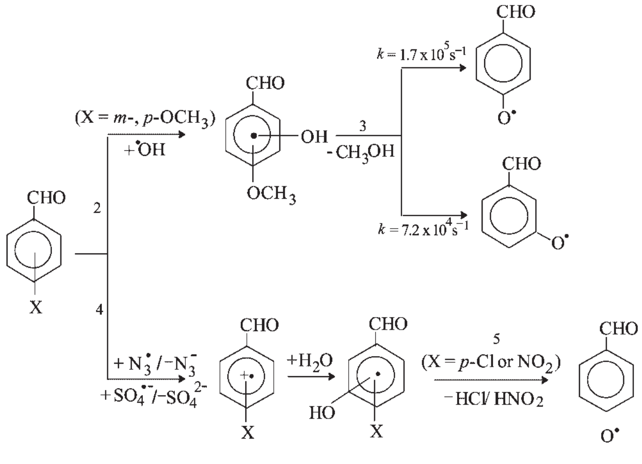
first step in the •OH reaction is the addition to the ring forming different isomeric of •OH adducts (reaction 1, Scheme 1).

The transient absorption spectra and their stabilities are found to depend on the substituent and the position. In *m*- and *p*-methoxybenzaldehydes, the initially formed •OH adducts decay to the corresponding phenoxyl radicals (reaction 3, Scheme 2). The first-order decay rates observed at 400–410 nm are attributed to the formation of the phenoxyl radical by demethoxylation (reaction 3, Scheme 2). The difference in the spectra of phenoxyl radicals of *m*- and *p*-substituted benzaldehydes are evident as the phenoxyl radicals of the *m*-isomers show two peaks whereas a single peak is observed in the case of phenoxyl radicals of the *p*-isomers. The first-order decay observed in the case of *p*-chlorobenzaldehyde suggests that the same mechanism is also operative.

Because $N_3^{\bullet}$ or $SO_4^{-\bullet}$ generally react by direct electron transfer, the formation of the radical cation (reaction 4, Scheme 2) is the initiating step. The radical cation then hydrolyses to form the corresponding •OH adducts. Of the possible six isomeric •OH adducts, the formation of the •OH adducts corresponding to the •OH attack at the *ipso* position of the substituents is more likely. The decay of absorption in the transient spectrum observed in the reaction with *p*-chlorobenzaldehyde and *p*-nitrobenzaldehyde is attributed to the formation of the phenoxyl radical (reaction 5, Scheme 2) by dechlorination/denitration of the •OH adducts.

CONCLUSION

The time-resolved spectral changes in the reaction of •OH with substituted benzaldehydes are interpreted in terms of phenoxyl radical formation via an addition reaction. The rate constants for the reaction of •OH with the substituted benzaldehydes are dependent on the nature and position of the substituent ($\rho^{+} = -0.4 \pm 0.09$), which further supports an addition reaction of •OH. The rates of formation of phenoxyl radical from the •OH adducts among the various derivatives seems to increase in the order *p*-hydroxy ($5.5 \times 10^{5}\,s^{-1}$) > *m*-hydroxy ($4.6 \times 10^{5}\,s^{-1}$) > *p*-methoxy ($1.7 \times 10^{5}\,s^{-1}$) > *m*-methoxy ($7.2 \times 10^{4}\,s^{-1}$) > *p*-nitro ($4.4 \times 10^{4}\,s^{-1}$). The reactions of $N_3^{\bullet}$ and $SO_4^{-\bullet}$ with the substituted benzaldehydes proceeds by electron transfer forming the intermediate radical cation, which hydrolyses to form the corresponding •OH adducts.



Scheme 2

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