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Radiation Chemical Oxidation of Benzaldehyde, Acetophenone, and Benzophenone

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Radiation chemical reactions of $^{\bullet}OH$, $O^{\bullet-}$, and $SO_4^{\bullet-}$ with benzaldehyde, acetophenone, and benzophenone have been studied using both pulse and steady-state radiolysis techniques. The observed rates for the $^{\bullet}OH$ addition ($k = (2.6-8.8) \times 10^9$ M^{-1} s^{-1}) are higher than those found for the $SO_4^{\bullet-}$ reaction ($k = (0.7-4.0) \times 10^9$ M^{-1} s^{-1}). The rate for the reaction of $O^{\bullet-}$ with benzaldehyde is higher than that found for $^{\bullet}OH$, while a reverse trend is observed in the case of the two ketones. Optical absorption spectra of the intermediate transients formed in the reactions of $^{\bullet}OH$ and $SO_4^{\bullet-}$ with all three compounds are similar with a peak around 370−380 nm. The absorption spectra from the $O^{\bullet-}$ reaction have shown a major peak at 310 nm and are somewhat different from those obtained in the reaction of $^{\bullet}OH$. The yields of the phenolic products formed in the reaction of $^{\bullet}OH$ with benzaldehyde and acetophenone in the presence of 0.1 mM ferricyanide corresponded to only 30% and 50% $^{\bullet}OH$ yields, respectively. Benzoic acid is a major product formed with benzaldehyde in the reaction of $^{\bullet}OH$ as well as $SO_4^{\bullet-}$ with G values of 2.1 and 1.3 per 100 eV, respectively. The formation of the exocyclic OH adduct is a major pathway in the reactions of $^{\bullet}OH$ (by addition) and of $SO_4^{\bullet-}$ from hydrolysis of the initially formed radical cation ($k = 2.4 \times 10^4$ s^{-1}) with benzaldehyde. The exocyclic OH adduct undergoes disproportionation to give benzoic acid. The formation of the exocyclic OH adduct of acetophenone is possibly hindered owing to the bulky $-COCH_3$ group.

Introduction

The radiation chemical reactions of water radicals (e_{aq}^-, $H^{\bullet}$, and $^{\bullet}OH$) and the secondary radicals (e.g., $SO_4^{\bullet-}$) derived from them with arenes in aqueous solution have been studied[1−4] using the pulse radiolysis technique since its advent more than 3 decades ago. These studies have been mainly concerned with the evaluation of kinetic parameters and measurement of transient absorption spectra with a view to obtain information on the rates and reaction mechanism. Owing to the precise knowledge of the yields of the primary radiolytic products of the radiolysis of water (reaction 1)

$$H_2O \rightsquigarrow e_{aq}^-, {}^{\bullet}OH, H^{\bullet}, H^+, H_2O_2, H_2 \qquad (1)$$

($G_{e_{aq}^-} = 2.8$, $G_{OH} = 2.8$, $G_H = 0.55$ per 100 eV energy absorbed) and owing to the limited solubility of arenes ($\leq 10^{-3}$ M) in water, the radiation chemical technique has been the method of choice for the generation of specific radicals, and it has thus proved to be an invaluable tool for studying the free radical chemistry of substituted benzenes. An important aspect of these studies has been the radiation chemical hydroxylation of substituted benzenes by the OH radical. In many cases, the detailed reaction mechanism, however, could not be reliably established, in the absence of product distribution data, entirely by time-resolved spectral studies because of competing parallel processes. Thus, to establish the reaction mechanism, the pulse radiolysis data need to be complemented by quantitative analysis of radiation products formed.

Modern chromatographic methods, particularly high-pressure liquid chromatography, now provide the radiation chemist with the capability of examining the product distribution in low yields. Schuler and co-workers[5−7] have pioneered the research in this area during the past 2 decades. We have undertaken, in the recent past, studies[8−10] on radiation chemical reactions of water radicals with various substituted benzenes, and of particular mention among them there has been a detailed investigation of the reactions of $^{\bullet}OH$ and $SO_4^{\bullet-}$ with chlorotoluenes[9] and cresols[10] by both pulse and steady-state radiolysis techniques. These studies have enabled us to quantify the relative rates of attack of $^{\bullet}OH$ at different positions of *o*-, *m*-, and *p*-chlorotoluenes.

The oxidation of benzaldehyde by potassium permanganate has been known for a very long time in the literature.[11−14] A free radical reaction mechanism involving the OH radical in basic solutions has been suggested[11] for this oxidation. Since radiation chemical methods are a clean source for $^{\bullet}OH$ generation, it is interesting to examine in detail the mechanism for radiation chemical oxidation of benzaldehyde. Although several studies[15] have been carried out on the photolysis of benzaldehyde, the mechanism for its radiation chemical oxidation has not been elucidated unlike its reaction with reducing water radicals.[16−20] We have employed in this work both pulse and steady-state radiolysis techniques to study the reactions of $^{\bullet}OH$, $O^{\bullet-}$, and $SO_4^{\bullet-}$ with benzaldehyde, acetophenone, and benzophenone.

Experimental Section

(A) Preparation of Solutions and Irradiations. Benzaldehyde, acetophenone, and benzophenone used in this study were obtained from Qualigens and SRL. Their purity (≥98%) was checked by HPLC, and they were used as received except benzaldehyde, which is known to undergo air oxidation to give benzoic acid. Purification of benzaldehyde was carried out by addition of ether and 10% sodium bicarbonate. The organic layer was dried over sodium sulfate. Ether was evaporated using

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a rotary evaporator, and the residue was distilled. The purified benzaldehyde was stored in an airtight bottle with a rubber septum to prevent it from oxidation, and the solutions were prepared just before use by withdrawing appropriate aliquots by a syringe. This procedure enabled us to inhibit its oxidation for at least 3−4 weeks. The purity of benzaldehyde was periodically checked by HPLC analysis prior to irradiation. Fresh solutions, prepared in water purified by the Millipore Milli-Q system, were used.

The amount of benzoic acid present in N_2O and N_2O/O_2-saturated solutions used for the $^{\bullet}$OH reaction and in N_2-saturated solutions in the presence of $S_2O_8^{2-}$ for studying the $SO_4^{\bullet-}$ reaction was less than 1%. Only in N_2O-saturated basic solutions (pH ≈ 13) was the extent of oxidation observed to be ∼25%. Hence, the studies in basic solutions were limited to pulse radiolysis. The HPLC chromatograms obtained for unirradiated solutions of benzaldehyde under different reaction conditions used in this study are shown along with those obtained following γ-radiolysis (cf. section C, Product Analysis). The concentrations of benzaldehyde and acetophenone for spectral measurements were usually kept at 1 mM. Owing to its limited solubility, the concentration of benzophenone was 0.1 mM. All the experiments were carried out at room temperature.

The reactions of $^{\bullet}$OH and $O^{\bullet-}$ were studied in N_2O-saturated solutions at pH 7 and 13, respectively, while the $SO_4^{\bullet-}$ radicals were produced by the reaction of e_{aq}^- and $H^{\bullet}$ with peroxydisulfate in N_2-saturated solutions containing 15 mM $K_2S_2O_8$ and 0.2 M *tert*-butyl alcohol.

High-energy electron pulses (7 MeV, 50 ns) from a linear accelerator were used for the experiments, and the details of the facility have been described elsewhere.[21,22] Dosimetry was carried out with aerated aqueous solutions of 10 mM KSCN solution by optical measurements, taking $G\epsilon_{500} = 21\,522$ M^{-1} cm^{-1} per 100 eV for the transient[23] $(SCN)_2^{\bullet-}$. A ^{60}Co source was employed for steady-state radiolysis experiments.

(B) Separation and Estimation of the Radiation Products. The HPLC system from Perkin-Elmer (Series 10 liquid chromatograph) coupled to an LC-235 photodiode array detector and reverse-phase Nucleosil C-18 (250 mm × 4.6 mm, Machery Nagel) or a Lichrospher 100 RP-18 column (125 mm × 4.6 mm, Merck) was used for the identification and estimation of the yields of the products formed from radiolysis of benzaldehyde and acetophenone. The radiation products were monitored at 220 (benzaldehyde) and 210 nm (acetophenone). The solvent was 30% acetonitrile in water, and a flow rate of 0.8 mL min^{-1} was used in the case of benzaldehyde while 30% methanol with a flow rate of 1.2 mL min^{-1} was used for acetophenone. The formation of benzoic acid was further confirmed by monitoring the chromatogram at 205 nm using water as the solvent and a flow rate of 1 mL min^{-1}. The standards were obtained commercially, and the products were characterized by their retention times and UV spectra. The concentration of the products was determined from the calibration curves of area versus concentration of the authentic samples. The *G* values were determined from the yield versus dose plots.

Results and Discussion

(A) Evaluation of Kinetic Parameters. *(i) Reaction of $^{\bullet}$OH.* The rates of the reaction of $^{\bullet}$OH with benzaldehyde, acetophenone, and benzophenone were determined from the buildup of the maximum absorption of the transients at 370−380 nm. The rates of formation were found to be first order and were observed to increase linearly with the solute concentration in the range 0.2−1 mM. The second-order rate constants for the reaction of $^{\bullet}$OH with benzaldehyde and benzophenone were determined from the slopes of k_{obs} versus [solute]. However, k_{obs} values were not determined as a function of [acetophenone] and the value was obtained from only one measurement. The *k* values obtained in this work along with those reported[1] earlier for some monosubstituted benzenes containing electron-donating or electron-withdrawing groups are shown in Table 1.

TABLE 1: Second-Order Rate Constants ($k/10^9$ M^{-1} s^{-1}) and λ_{Max}/nm Obtained in the Reactions of $^{\bullet}$OH, $O^{\bullet-}$, and $SO_4^{\bullet-}$ with Benzaldehyde, Acetophenone, and Benzophenone and with Some Other Monosubstiuted Benzenes[a]

	$^{\bullet}$OH		$O^{\bullet-}$	$SO_4^{\bullet-}$
substrate	*k*	λ_{max}	*k*	*k*
benzaldehyde	2.6 ± 0.3 (4.4)[24]	370	5.5 ± 0.6	0.71 ± 0.055
acetophenone	3.7 (5.4)[25]	370	0.9 ± 0.12	1.8 ± 0.1 (0.31)[28]
benzophenone	7.7 ± 1.1 (9.0)[18]	380	1.1 ± 0.15	4.0 ± 0.5
anisole	5.4	330	nd	4.9
toluene	3.0	313	2.1	3.1
benzonitrile	4.4	348	0.07	0.12
nitrobenzene	3.9	410	nd	≤0.001

[a] nd—not determined. Values of the rate constants for anisole, toluene, benzonitrile and nitrobenzene are taken from refs 1 ($^{\bullet}$OH and $O^{\bullet-}$), 2, and 28 ($SO_4^{\bullet-}$).

Our value of $k = (2.6 \pm 0.3) \times 10^9$ M^{-1} s^{-1} for benzaldehyde is less than that reported earlier (4.4×10^9 M^{-1} s^{-1}) by Shevchuk et al.[24] This discrepancy may be due to the difference in the methods employed, since the latter determined their value by the indirect method of competition kinetics. Our value ($k = (7.7 \pm 1.1) \times 10^9$ M^{-1} s^{-1}) for benzophenone is in reasonable agreement with that reported (9.0×10^9 M^{-1} s^{-1}) by Brede et al.[18] The *k* value of 3.7×10^9 M^{-1} s^{-1} in the case of acetophenone is between the values obtained for benzaldehyde and benzophenone. However, it is lower than the value ($k = 5.4 \times 10^9$ M^{-1} s^{-1}) reported by Wilson et al.[25]

The observed *k* values with all three systems indicate that the rates are nearly diffusion controlled. The increase in the values on going from benzaldehyde to benzophenone is in accord with the increase in electron density due to the replacement of $-H$ by $-CH_3$ or $-C_6H_5$ in the functional group. The rate constant for the $^{\bullet}$OH reaction with benzaldehyde is similar to that reported[1] for toluene, while those for acetophenone and benzophenone are comparable to nitrobenzene and anisole, respectively (Table 1). It is, therefore, evident that there is no significant effect of substituent on the reactivity of $^{\bullet}$OH with monosubstituted benzenes unlike in the case of substituted purines, the respective ρ^+ values[26,27] being −0.5 and −2.5.

(ii) Reaction of $O^{\bullet-}$. Similar to the $^{\bullet}$OH reaction, the second-order rate constants for the reaction of $O^{\bullet-}$ were determined by monitoring the formation of the transients at the $\lambda_{max} = 310$ nm. As mentioned in the Experimental Section, not more than 25% of benzaldehyde was oxidized to benzoic acid in unirradiated basic solutions (pH ≈ 13) on the time scale (≤2 h) of our experiments. Thus, the amount of benzoic acid present in unirradiated solutions for the highest [benzaldehyde] used in our study (1 mM) was not more than 0.25 mM. The reported[1] upper limit of the rate constant for the reaction of $O^{\bullet-}$ with benzoic acid is 4.0×10^7 M^{-1} s^{-1}. Based on the reactivities of $O^{\bullet-}$ with benzaldehyde ($k_{obs} = k[\text{solute}] = 7.2 \times 10^4$ s^{-1}) and benzoic acid ($k_{obs} = 1.0 \times 10^4$ s^{-1}), it is seen that nearly 90% of $O^{\bullet-}$ reacted with benzaldehyde. Thus, the rate constants measured in our work indeed represent those for the $O^{\bullet-}$ reaction with benzaldehyde.

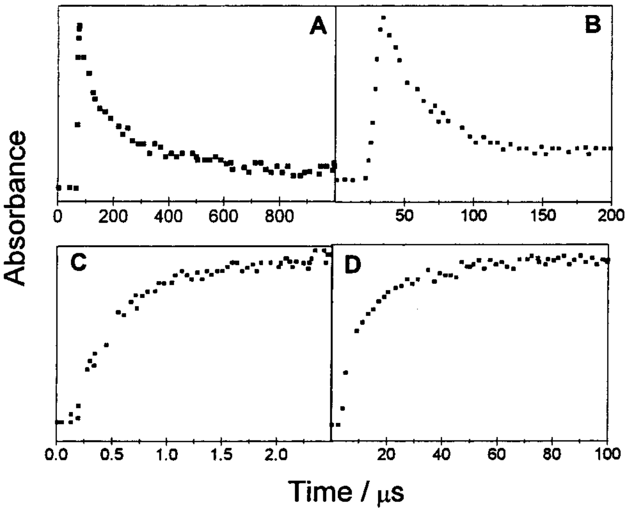


Figure 1. Different traces obtained in this work for decay at (A) 370 nm and (B) 350 nm obtained in the reactions of $^{\bullet}OH$ and $SO_4^{\bullet-}$ with benzaldehyde, respectively. Buildup (λ_{max} = 310 nm) at (C) 2.5 μs and (D) 100 μs was measured in the reaction of $O^{\bullet-}$ with benzaldehyde. Dose per pulse = 1.5 krad; [benzaldehyde] = 1 mM.

The rate of buildup at 310 nm with benzaldehyde has shown an initial fast growth followed by a fall-off of the rate, indicating a change in reaction mechanism (cf. section D). The traces recorded on a 2.5 and 100 μs scale are shown in Figure 1. The rate of the former was found to be linearly dependent on [benzaldehyde] and the second-order rate constant evaluated from this is (5.5 ± 0.6) × 10^9 M^{-1} s^{-1}. The rate of the latter from the trace recorded using 1 mM solutions is 4.3 × 10^4 s^{-1}. Such a behavior was, however, not observed in the case of acetophenone and benzophenone. The rate constants evaluated from the linear k_{obs} versus [solute] plots for the $O^{\bullet-}$ reaction with acetophenone and benzophenone are nearly equal, the respective values being (9.0 ± 1.2) × 10^8 and (1.10 ± 0.15) × 10^9 M^{-1} s^{-1}. The rate of the $O^{\bullet-}$ reaction with benzaldehyde was found to be higher than that for the $^{\bullet}OH$, while a reverse trend is seen in the case of acetophenone and benzophenone.

The higher reactivity of $O^{\bullet-}$ with benzaldehyde compared to that with the two ketones could be due to the different mechanism by which it reacts. The major pathway for its reaction with benzaldehyde is by H abstraction from the aldehyde group, while addition to the benzene ring predominates in the case of acetophenone and benzophenone. The decrease in rates of the $O^{\bullet-}$ reaction relative to the $^{\bullet}OH$ in the case of acetophenone and benzophenone is due to the nucleophilic nature of $O^{\bullet-}$.

(iii) Reaction of $SO_4^{\bullet-}$. The second-order rate constants obtained for the reaction of $SO_4^{\bullet-}$ with benzaldehyde, acetophenone, and benzophenone are (7.10 ± 0.55) × 10^8, (1.8 ± 0.1) × 10^9, and (4.0 ± 0.5) × 10^9 M^{-1} s^{-1}, respectively. Our rate constant value for the $SO_4^{\bullet-}$ reaction with acetophenone is 6 times higher than that reported by Neta et al.,[28] and the reason for this difference is not clear. Electron-withdrawing groups cause deactivation of the benzene ring for the $SO_4^{\bullet-}$ attack, and hence, substituted benzenes containing electron-withdrawing substituents have apparently low reactivity with $SO_4^{\bullet-}$. The increase in the *k* value on going from benzaldehyde to benzophenone is due to the decrease in the deactivation of the benzene ring for the $SO_4^{\bullet-}$ attack. The large difference in the magnitude of observed *k* values for the $^{\bullet}OH$ and $SO_4^{\bullet-}$ reactions is in line with the relatively stronger electrophilic nature of $SO_4^{\bullet-}$ ($\rho^+ = -2.5$) found[28] in its reaction with monosubstituted benzenes.

(B) Transient Absorption Spectra. *(i) Reaction of $^{\bullet}OH$ and $O^{\bullet-}$ Radicals.* Optical absorption spectra of the intermediate transients formed in the reaction of $^{\bullet}OH$ with benzaldehyde were

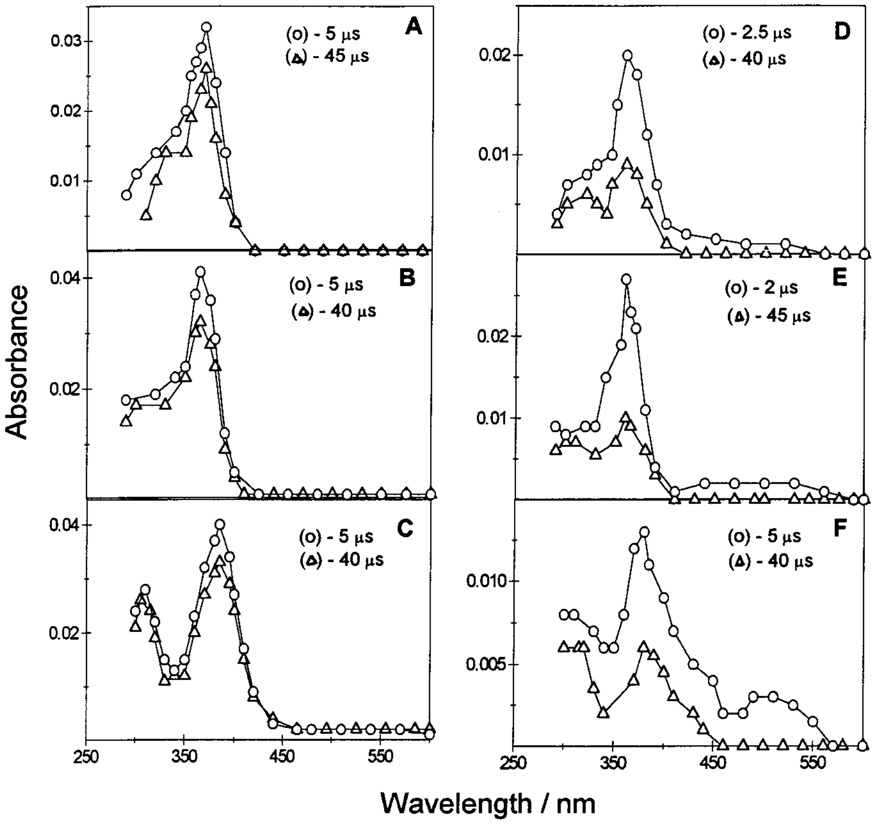


Figure 2. Time-resolved absorption spectra obtained in the reactions of $^{\bullet}OH$ (A−C) and $SO_4^{\bullet-}$ (D−F) with 1 mM benzaldehyde (A and D), 1 mM acetophenone (B and E), and 0.1 mM benzophenone (C and F).

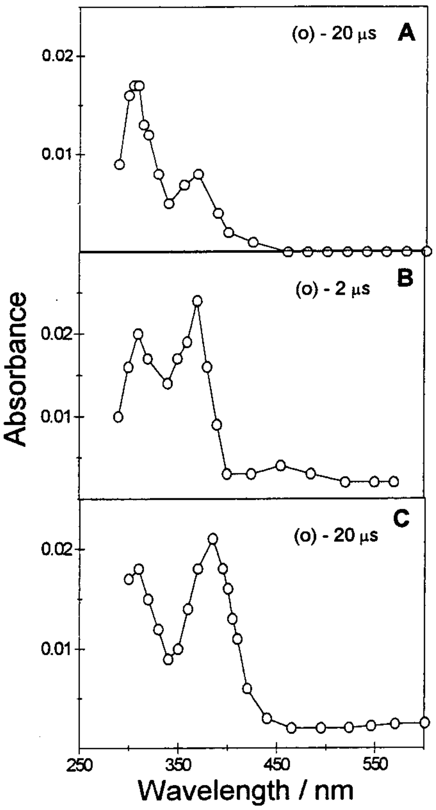


Figure 3. Time-resolved absorption spectra obtained in the reactions of $O^{•-}$ with (A) 1 mM benzaldehyde, (B) 1 mM acetophenone, and (C) 0.1 mM benzophenone.

monitored in the range 280−600 nm. In Figure 2 is shown the transient absorption spectrum obtained in N_2O-saturated neutral solutions of benzaldehyde (1 mM) after completion of the reaction (5 μs after the pulse). The spectrum exhibited a peak at 370 nm with a shoulder around 310 nm. The spectra obtained for the transients formed in acetophenone and benzophenone are also similar with characteristic peaks at 370 nm, though the shoulder at 310 nm in the benzaldehyde transient spectrum transformed into a peak in benzophenone. Such a transformation is not, however, apparent in the case of acetophenone (Figure 2). The absorption spectra obtained for acetophenone and benzophenone are similar to those reported in the literature.[26,29] The λ_{max} in all the three systems is red-shifted by nearly 50 nm compared to the λ_{max} of substituted benzenes (e.g., anisole and toluene)[30] with electron-donating groups. Such a shift,[26] which was also noticed in the OH adducts of benzonitrile and nitrobenzene, is due to the extended conjugation in these systems. The time-resolved spectrum recorded at 45 μs after the pulse has shown the usual bimolecular decay of the transients.

Pulse radiolysis experiments were also carried out in N_2O-saturated solutions of these compounds at pH 13 in order to ascertain the differences in the mechanism of the $^•OH$ and $O^{•-}$ reactions. The spectra after the completion of the reaction for the three systems are shown in Figure 3, which are somewhat different from those obtained in its reaction with OH radicals. As can be seen from Figure 3, the absorption spectra obtained in the $O^{•-}$ reaction exhibited an intense peak at 310 nm and a weaker one at 370 nm in the case of benzaldehyde, the ratio of the intensities being 3:1. The intensities of the two peaks are, however, nearly equal in the case of acetophenone and benzophenone.

(ii) Reaction of $SO_4^{•-}$. The transient absorption spectrum measured in the $SO_4^{•-}$ reaction with benzaldehyde, shown in Figure 2, is similar to that obtained in its reaction with $^•OH$, i.e., with a peak at 370 nm and a shoulder at 310 nm. In addition, a very weak absorption in the region between 450 and 480 nm was observed in the $SO_4^{•-}$ reaction. The spectra with acetophenone and benzophenone (Figure 2) are more or less similar, though the intensities of the absorption at 370 nm were different. The order for the intensities found is acetophenone > benzaldehyde > benzophenone. An important difference in the $^•OH$ and $SO_4^{•-}$ reactions is the variation in the rates of the decay of the absorption at 370 nm. The decay is much faster in the latter than in the former, as can be seen from the traces shown in Figure 1 for the benzaldehyde system. Note that the time scales of the decay are 1000 and 200 μs for the $^•OH$ and $SO_4^{•-}$ reactions, respectively. The rate of decay from the trace obtained in the $SO_4^{•-}$ reaction was found to be first order, and the k value obtained from the trace is 2×10^4 s^{-1}. The decay rate for the $^•OH$ reaction is at least 5 times lower and is ascribed to the usual bimolecular decay of the transients.

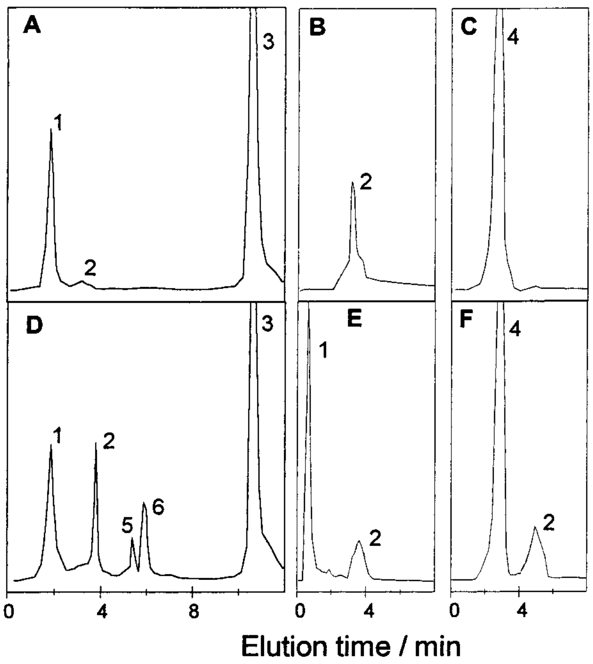


Figure 4. HPLC chromatograms obtained for unirradiated (A−C) and ^{60}Co γ-irradiated (D−F) benzaldehyde solutions (1 mM): (A, D, and E) N_2O-saturated solutions containing $K_3Fe(CN)_6$ (0.1 mM); (B) at pH ≈ 13; (C and F) N_2-saturated solutions containing potassium persulfate (15 mM) and *tert*-butyl alcohol (0.2 M); (A−D and F) 220 nm, eluent—30% acetonitrile in water; (E) 205 nm, eluent—100% water; (peak 1) ferricyanide; (peak 2) benzoic acid; (peak 3) benzaldehyde; (peak 4) potasssium persulfate; (peak 5) *p*-hydroxybenzaldehyde; (peak 6) *m*-hydroxybenzaldehyde. Dose = 20 krad.

(C) Product Analysis. The major stable products formed in the $^•OH$ reaction with substituted benzenes are the corresponding phenols. Most commonly employed oxidants are $Fe(CN)_6^{3-}$ ($E° = 360$ mV),[31] $IrCl_6^{2-}$ ($E° = 870$ mV),[31] and methylviologen ($E° = -448$ mV).[31] All three oxidants were used in our experiments for the oxidation of the OH adducts of benzaldehyde.

The HPLC chromatograms for the unirradiated solutions under different conditions are shown in parts A−C of Figure 4. The chromatogram of the unirradiated solution obtained in the reaction of $^•OH$ with benzaldehyde in the presence of 0.1 mM ferricyanide has shown two major peaks corresponding to the ferricyanide and benzaldehyde (peaks 1 and 3 in Figure 4A) and also a very small peak due to benzoic acid (peak 2) whose concentration was estimated as $\leq 1 \times 10^{-5}$ M accounting for an impurity level of ≤1%. Furthermore, the peak of benzal-

TABLE 2: Yields per 100 eV of Products Formed in ^{60}Co γ-Radiolysis Following the $^{\bullet}$OH and $SO_4^{\bullet-}$ Reactions with Benzaldehyde and Acetophenone under Different Solution Conditions[a]

	$^{\bullet}$OH			
	N_2O	N_2O 0.1 mM $Fe(CN)_6^{3-}$	N_2O/O_2 (4:1) (v/v)	$SO_4^{\bullet-}$
(A) Benzaldehyde				
benzoic acid	1.8	2.1 (1.0)	2.1	1.3
m-hydroxybenzaldehyde	0.2	0.8 (1.2)	0.2	nf
p-hydroxybenzaldehyde	0.1	0.4 (0.5)	0.1	nf
(B) Acetophenone				
o-hydroxyacetophenone	nf	0.6 (2.0)	nf	nd
m-hydroxyacetophenone	trace	1.6 (1.5)	0.4	nd
p-hydroxyacetophenone	0.1	0.6 (0.6)	0.3	nd

[a] nd—not determined. nf—not formed. The values in parentheses are obtained in the presence of $IrCl_6^{2-}$.

dehyde in unirradiated solution shows a small hump whose area is negligible. This may be due to some impurity level of $\leq 10^{-7}$ M. No increase in the area of this peak was seen with dose, and only at doses ≥ 30 krad was a slight increase in its peak area noticed.

The products formed in the ^{60}Co γ-radiolysis of N_2O-saturated solutions of benzaldehyde in the absence of any oxidant were identified as benzoic acid and *m*- and *p*-hydroxybenzaldehydes, and the estimated *G* values are tabulated in Table 2. *o*-Hydroxybenzaldehyde was found to be eluted within 1 min after benzaldehyde, and its formation was not observed as can be seen from the chromatograms recorded in Figure 4. Even if the impurity trace noticed in the benzaldehyde peak is ascribed to *o*-hydroxybenzaldehyde, its yield as a radiolytic product must be negligible. The *G* value of benzoic acid in deoxygenated solutions was found to be 1.8 per 100 eV, whereas the yields of phenolic products are marginal. Although the yields of *m*- and *p*-hydroxybenzaldehydes were enhanced in the presence of ferricyanide, the *G* value of benzoic acid remained more or less unaffected. Their yields were estimated to be 0.8, 0.4, and 2.1 per 100 eV, respectively.

The HPLC chromatogram of the products formed in the γ-radiolysis of N_2O-saturated solutions of benzaldehyde in the presence of ferricyanide for a typical dose of 20 krad is depicted in Figure 4D, and the peaks marked 2, 5, and 6 correspond to benzoic acid and *p*- and *m*-hydroxybenzaldehydes, respectively. The formation of benzoic acid as a radiation product, as mentioned earlier, was further confirmed using 100% water as the solvent and by monitoring it at 205 nm. The chromatogram obtained from radiolysis using this solvent has shown a single peak due to benzoic acid (Figure 4E). The phenolic products, however, could not be separated using this solvent. When ferricyanide was replaced by a less powerful oxidant, methylviologen, *m*- and *p*-hydroxybenzaldehydes were not at all formed, whereas their yields were slightly enhanced (*G*(total) = 1.7) when $IrCl_6^{2-}$ was used. Trace amount of *o*-hydroxybenzaldehyde was formed in the presence of $IrCl_6^{2-}$. The yields of phenols with benzaldehyde are among the lowest found for substituted benzenes containing electron-withdrawing substituents. For instance, the total phenolic yields in benzonitrile in the presence of $Fe(CN)_6^{3-}$ are reported[32] to be 85% $^{\bullet}$OH yield.

The chromatogram recorded in N_2O/O_2 (4:1)-saturated solutions of benzaldehyde following γ-radiolysis (not given in figure) has shown the formation of the same products with nearly identical yields as in N_2O-saturated solutions. In its reaction with $SO_4^{\bullet-}$, the formation of only benzoic acid with a *G* value of 1.3 was observed (Figure 4F).

The HPLC analysis of the products formed in the γ-radiolysis of N_2O-saturated solutions of acetophenone in the presence of ferricyanide has shown the formation of three major products that were identified as the hydroxy isomers of acetophenone. The *G* values of *o*-, *m*-, and *p*-hydroxyacetophenones were found to be 0.6, 1.6, and 0.6 per 100 eV, respectively. In the presence of $IrCl_6^{2-}$, the yields of *m*- and *p*-hydroxyacetophenones remained the same while that of *o*-hydroxyacetophenone increased by about 3 times. In N_2O/O_2 (4:1)-saturated solutions, negligible amounts of *m*- and *p*-isomers were formed while the formation of *o*-hydroxyacetophenone was not observed (Table 2).

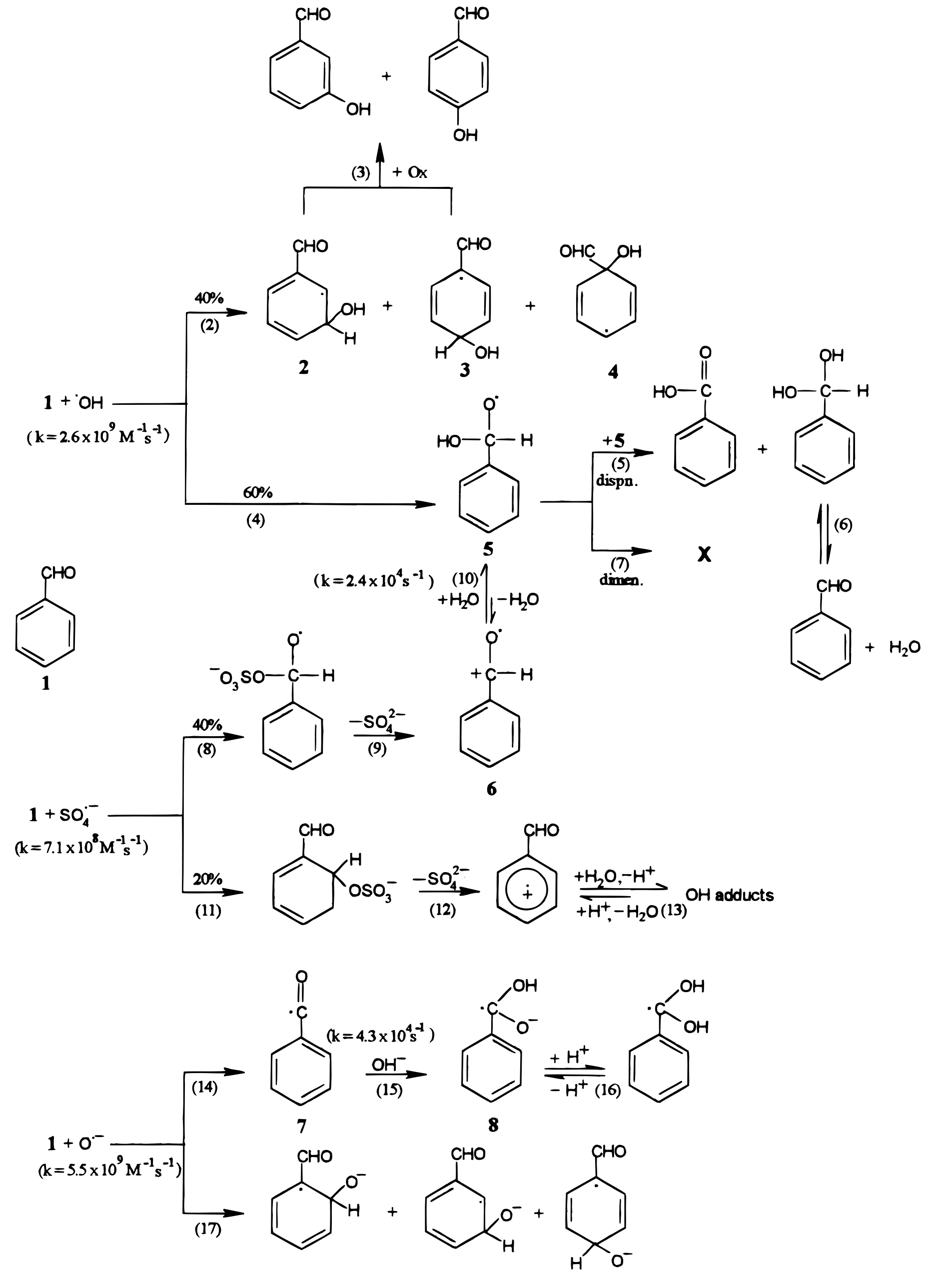
(D) Reaction Mechanism. The different OH adducts that can be formed in the reaction of $^{\bullet}$OH with benzaldehyde are shown in Scheme 1. These can arise from the attack of $^{\bullet}$OH on the ring (reaction 2) and on the −CHO group (reaction 4). The attack of $^{\bullet}$OH on the ortho position of benzaldehyde must be negligible as is evident from the lack of formation of salicylaldehyde under steady-state conditions. The two hydroxycyclohexadienyl radicals (structures 2 and 3) except the ipso OH adduct (structure 4) can be oxidized to the corresponding phenols in the presence of an oxidant (reaction 3). Since the yields of the phenolic products correspond to 30% $^{\bullet}$OH yield, the ipso adduct formation is limited to 10% $^{\bullet}$OH yield. Buxton et al.[33] have shown that the rate of oxidation of the OH adducts of substituted benzenes by ferricyanide is dependent on the substituent with the second-order rate constants varying from 2.3×10^9 M^{-1} s^{-1} for anisole to about 5×10^6 M^{-1} s^{-1} for chlorobenzene ($\rho^+ = -3.0$). They have further shown that the behavior with the stronger oxidant $IrCl_6^{2-}$ has not revealed any electronic effects of the substituent with the rates close to diffusion controlled, except in the case of the OH adducts of benzonitrile[33] where $k = 4.5 \times 10^8$ M^{-1} s^{-1}.

Since the yields of the phenolic products formed from benzaldehyde are very low, even in the presence of the oxidants, pulse radiolysis experiments to evaluate the rates of oxidation of the OH adducts by ferricyanide were not attempted. However, it is assumed that the rates of oxidation of the hydroxy adducts of benzaldehyde by $IrCl_6^{2-}$ must be comparable to those found for benzonitrile. It is thus expected that their quantitative conversion to the corresponding phenols under γ-radiolysis occurs. The yields of the hydroxybenzaldehydes measured in the presence of $IrCl_6^{2-}$ must then represent the extent of initial $^{\bullet}$OH attack. Since the combined *G* value of *m*- and *p*-hydroxybenzaldehydes in N_2O-saturated solutions in the presence of $IrCl_6^{2-}$ is 1.7, only 30% $^{\bullet}$OH seems to add to the ring.

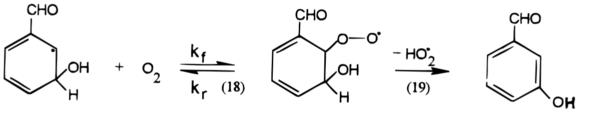
The reason for low phenolic yields in the case of benzaldehyde is the possibility of another reaction channel leading to the formation of the exocyclic OH adduct (structure 5) from the addition of $^{\bullet}$OH to the carbonyl group of benzaldehyde (reaction 4). The total yields of hydroxybenzaldehydes and benzoic acid account for about 90% $^{\bullet}$OH yield. The interesting finding is that the *G* values of benzoic acid are more or less the same with and without any oxidant (2.1 and 1.8 per 100 eV, respectively). Radiation chemical oxidation of benzaldehyde to benzoic acid is interpreted in terms of the disproportionation of the exocyclic OH adduct (structure 5) to give benzoic acid (reaction 5), which can account for the complete consumption of $^{\bullet}$OH. Dimerization of this adduct seems to be a minor process.

The addition of O_2 to the OH adducts of benzene and its derivatives has been reported[32] to be reversible, and $HO_2^{\bullet}$ elimination from the peroxyl radical results in the formation of the corresponding phenol. Considering one of the OH adducts

SCHEME 1



of benzaldehyde as an example, this process is shown in reactions 18 and 19:



The yields in oxygenated solutions of benzene derivatives are usually lower[9e,32] than in deoxygenated solutions in the presence of an oxidant other than O_2, especially with derivatives containing electron-withdrawing groups. This is due to the low values of K $(=k_f/k_r) \leq 1$ and the rate of $HO_2^{\bullet}$ elimination. This possibly explains the significant reduction in the yields of the hydroxybenzaldehydes in the presence of O_2.

The proposed mechanism for the formation of benzoic acid from the disproportionation of the exocyclic OH adduct (structure 5) is also in accord with the observed yields of benzoic acid (G = 1.3) in the $SO_4^{\bullet-}$ reaction under steady-state conditions (Table 2). The radical cation (structure 6) formed by addition−elimination and/or direct electron-transfer from the −CHO group is hydrolyzed in neutral solutions to give the corresponding exocyclic OH adduct (reaction 10). As in the case of the $^{\bullet}$OH reaction, this OH adduct disproportionates to give benzoic acid (reaction 5) that will account for the consumption of 80% $SO_4^{\bullet-}$ yield. The $SO_4^{\bullet-}$ attack (reaction 11) on the ring seems to be a marginal process, and it occurs only to an extent of 20%.

Thus, the $^{\bullet}$OH and $SO_4^{\bullet-}$ addition to the carbonyl group seems to predominate over addition to the benzene ring. The proposed mechanism is also in accord with the transient absorption spectrum measured in the $SO_4^{\bullet-}$ reaction. The initial spectrum with λ_{max} at 350 nm (Figure 2) is assigned to the radical cation (structure 6) formed in reaction 9, and the first-order decay (2.4×10^4 s^{-1}) is attributed to the formation of the exocyclic OH adduct (reaction 10). The exocyclic adduct is not expected to absorb above 300 nm. The rate of hydrolysis of radical cation 6 ($k = 2.4 \times 10^4$ s^{-1}) must be relatively slower than the corresponding value for the σ adduct radical.

The reaction of $O^{\bullet -}$ seems to proceed mainly through H abstraction from the aldehyde group (reaction 14), leading to the radical **7**. This is evident from the peak observed at 310 nm in the transient absorption spectrum. The decrease in the rate of absorption at 310 nm is ascribed to the attack of radical **7** by OH^-. This radical in the presence of high $[OH^-]$ leads to the radical anion **8**. The relatively less intense peak at 370 nm is assigned to the addition of $O^{\bullet -}$ to the benzene ring (reaction 17).

The proportion of the yields of ortho:meta:para isomers of phenolic products formed in radiolysis of acetophenone in the presence of 0.1 mM ferricyanide is 0.5:1.3:1 per position (Table 2). When 0.2 mM $IrCl_6^{2-}$ was used as the oxidant, the G value of the ortho isomer was enhanced from 0.6 to 2.0, giving a proportion of 1.6:1.3:1 per position for ortho, meta, and para isomers, respectively, with the total phenolic yield ($G = 4.1$) corresponding to 75% $^\bullet OH$ yield. $IrCl_6^{2-}$, being a stronger oxidant than $Fe(CN)_6^{3-}$, must be able to oxidize all the OH adducts formed from its attack. The other two possible channels, i.e., addition to the ipso carbon and the functional group $-COCH_3$, together should account for the remaining 25% $^\bullet OH$ yield. Assuming that the extent of $^\bullet OH$ attack at these two positions is equally likely, the proportion of the yields of ortho:meta:para:ipso:exo (1.6:1.3:1:1.1:1.1) indicates that there is not much preference for $^\bullet OH$ addition to any of these positions. It seems that the formation of the exocyclic OH adduct of acetophenone compared to benzaldehyde is hindered owing to the bulky $-COCH_3$ group.

Conclusions

The $^\bullet OH$ addition to the functional group of benzaldehyde seems to predominate over addition to the benzene ring, leading to the formation of the exocyclic OH adduct, while addition to the ring is predominant in the case of acetophenone. Benzoic acid is a major product formed in both the $^\bullet OH$ and $SO_4^{\bullet -}$ reactions, and its formation has been explained by disproportionation of the exocyclic OH adduct. The major reaction pathway for the reaction of $O^{\bullet -}$ with benzaldehyde is by H abstraction from the aldehyde group, while addition to the ring predominates in the case of both the ketones. This study demonstrates the usefulness of radiation chemical methods in the elucidation of the oxidation reaction mechanism of aromatic aldehydes.

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