RADIATION INDUCED DEGRADATION OF WATER POLLUTANTS

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Abstract

Radiation chemical oxidation of hydroxybenzaldehydes, cresols and chlorotoluenes have been studied using both pulse and steady-state radiolysis techniques. The rates of the reaction of $^{\bullet}$OH were found to be high. Dehydration leading to the formation of the phenoxyl radical was observed from the OH adducts of *m*-hydroxybenzaldehyde. The rates of oxygen addition to the OH adducts of *o*-, *m*- and *p*-chlorotoluenes and cresols are high. The relatively high stability constants of peroxyl radicals formed with cresols than with chlorotoluenes suggest that the product forming reaction competes effectively with the reverse reaction in cresols.

INTRODUCTION

The reactions of the primary water radicals and secondary radicals derived from them with substituted benzenes in aqueous solution are of current interest. An important aspect well addressed in the recent past is the radiation chemical hydroxylation of benzenes and also their oxidative degradation using radiation. [1,2] Owing to the precise knowledge of the yields of the primary radiolytic products of water and limited solubility of arenes radiation chemical technique is best suited for these studies.

These studies have been carried out with a view to gain further insight into the radiation chemical oxidation of hydroxybenzaldehydes and cresols and also the reaction of oxygen with the OH adducts of cresols. Also information on the structure-reactivity correlation can be obtained.

METHODOLOGY

All the chemicals used in the present study were of high purity. The solutions were freshly prepared in water purified by the Millipore Milli-Q system.

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 peroxydisulphate in N_2 saturated solutions containing *tert*-butyl alcohol.

High energy electron pulses (7 MeV, 50 ns) from a linear accelerator were used for the experiments. Steady-state experiments were performed using a ^{60}Co γ-source. For the product analysis HPLC system coupled to a diode array detector was used.

RESULTS AND DISCUSSION

1. Reaction of $^{\bullet}$OH with Hydroxybenzaldehydes

The rate constants for the reaction of $^{\bullet}$OH with *m*- and *p*-hydroxybenzaldehydes were determined to be nearly diffusion-controlled (Table 1). The absorption spectra in N_2O saturated solutions of *m*-hydroxybenzaldehyde exhibited a single peak at 400 nm. Figure 1 depicts the time-resolved spectra measured at 1.5 and 15 μs after the pulse. As can be seen from the figure, a considerable decrease in intensity at 400 nm with a corresponding increase in absorption at 500 nm was noticed 15 μs after the pulse. The rate for the growth of absorption at 500 nm was estimated to be $1.5 \times 10^{5}\ s^{-1}$. The increase in absorption at 500 nm is attributed to the elimination of water leading to the formation of phenoxyl radical. The dehydration reaction from the OH adducts of substituted phenols and substituted purines has been reported earlier. [3,4]

The spectral nature of the transients formed in the reaction of $^{\bullet}$OH with *p*-hydroxybenzaldehyde is different than that recorded for the meta isomer. In addition to a peak around 400 nm, a very intense peak at 325 nm was seen, the ratio of the respective intensities being 1:4. The absorbance at 325 nm decreases rapidly and is linearly dependent on [*p*-OHC_6H_4CHO]. This fast decrease is ascribed to the reaction of the exocyclic OH adduct with *p*-hydroxybenzaldehyde.

2. Peroxyl radical chemistry of cresols and chlorotoluenes

The rates for the reaction of $^{\bullet}$OH with *o*-, *m*- and *p*-cresols, listed in Table 1, are the highest among those found for disubstituted benzenes. The transient absorption spectra exhibited peaks at 295 nm in the case of *o*-cresol and at 325 and 305 nm for meta and para isomers respectively.

The rates of oxygen addition to OH adducts of cresols are high, with the k_f values lying in the range 1 - 2.7×10^8 M^{-1} s^{-1}. The stability constants ($K = k_f / k_r$) of the peroxyl radicals formed with cresols are higher than those for chlorotoluenes suggesting that the product forming reaction competes effectively with the reverse reaction in cresols.

The products formed in the reaction of $^{\bullet}$OH with *o*-, *m*- and *p*-chlorotoluenes in the presence of oxygen (N_2O/O_2 [4:1]) were separated by HPLC. It was observed that the yields of the phenolic products were reduced by more than 80% in the presence of oxygen. Dihydroxytoluenes with –OH groups ortho to each other were formed in oxygenated solutions of cresols. The formation of such isomers of cresols is possible only from 1,3-type peroxyl radicals when the radical site is localized at the carbon carrying the –OH group.

As is known phenolic products can be formed from $HO_2^{\bullet}$ elimination from only 1,3-cyclohexadienyl peroxyl radicals, whereas 1,4-type radicals result in endoperoxidic products. It was observed that the yields of the phenolic products are higher in the case of cresols compared to *m*- and *p*-chlorotoluenes suggesting that the rates of $HO_2^{\bullet}$ elimination and other product forming reactions are higher in cresols than in the case of *m*- and *p*-chlorotoluenes. This is also substantitated by larger values of stability constant.

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Table 1 : Bimolecular rate constants (10^9 M^{-1} s^{-1}) and λ_{max} (nm) obtained in the reaction of $^{\bullet}$OH with some disubstituted benzenes

	λ	*k*
o-cresol	295	3.4
m-cresol	325	3.8
p-cresol	305	6.1
m-hydroxybenzaldehyde	400	7.7
p-hydroxybenzaldehyde	325 410	7.5 5.0

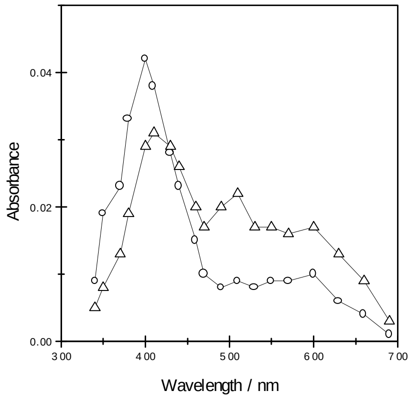

Figure 1: Time-resolved spectra obtained in the reaction of $^{\cdot}$OH with meta hydroxybenzaldehyde, 1.5 (O) and 15 µs (Δ) after the pulse