PULSE RADIOLYSIS STUDIES OF 3-HYDROXYBENZYL ALCOHOL

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ABSTRACT

Pulse radiolysis studies of 3-hydroxybenzyl alcohol (3-HBA) were carried out at various pHs. At pH 6.8 OH radicals were found to react with 3-HBA (k = 2 x 10⁹ dm³ mol⁻¹ s⁻¹) giving an species having absorption maximum at 340 nm, which decayed by unimolecular process (k₁ = 1.5 x 10⁵ s⁻¹) to another transient species having absorption maxima at 290 and two closely lying peaks at 390 and 410 nm. Latter time window spectrum is assigned to phenoxyl radicals by comparing spectrum of the species formed in reaction of N₂⁻ radicals with 3-HBA. At pH 6.8, decay of OH adduct as well as formation rate of phenoxyl radicals were found to increase with buffer ion concentrations. At pH 6.8, in addition to adduct species, OH radicals were found to abstract H-atoms from –CH₂OH group giving reducing radicals. At pH 1, reaction of OH radicals (k = 4 x 10⁹ dm³ mol⁻¹ s⁻¹) with 3-HBA, exclusively gives phenoxyl radical as confirmed by the formation of identical species in the reaction with Cl⁻ radicals. At pH 13.3, where 3-HBA exists in anionic form, reaction of O⁻ radicals was found to give a mixture of phenoxyl radicals and reducing radicals by H-abstraction from –CH₂OH group. H-atoms also reacted with 3-HBA (k = 3 x 10⁹ dm³ mol⁻¹ s⁻¹ giving the transient species (λmax = 330 nm) which were capable of reducing methylviologen quantitatively, suggesting that H-atoms also abstract H-atom from –CH₂OH group 3-HBA.

Introduction

There have been reports that hydroxybenzyl alcohols (HBA) that are biologically important molecules, are very good free radical scavengers. However, there are no studies on kinetic and mechanism of their free radical induced oxidation activities. Reactions of OH radicals give adduct species, which in turn decay to phenoxyl radicals depending on the nature of substitution. Due to the presence of phenolic OH group and –CH₂OH group in HBA, reactions of hydroxyl radical with HBA, can take place either by addition pathway, one electron oxidation as well as H-atom abstraction. In connection with earlier studies carried out on radiolytic reactions of 2-hydroxybenzyl alcohol and 4-hydroxybenzyl alcohol, studies on their isomer viz. 3-hydroxybenzyl alcohol (3-HBA) were carried out, to have structure-reactivity relationships. We have characterized the transient species formed at various pHs in the reactions with of .OH/O⁻ radicals with
3-HBA-based on spectral characteristics and comparison with phenoxy radicals generated exclusively with specific oxidants such as N3, and a suitable reaction mechanism is given in this paper.

**Experimental**

3-hydroxybenzyl alcohol (3-HBA) was obtained from Fluka Co and was used as such. Solutions were prepared using water from Millipore A-10 system having conductivity less than 0.1 $\mu$S/cm. Gases such as $N_2$, $O_2$, and $N_2O$ used for saturating the solutions were of IOLAR/Instrument grade from Indian Oxygen Ltd. pH of the solutions were adjusted using NaOH, HClO$_4$, KH$_2$PO$_4$, and Na$_2$HPO$_4$ at appropriate concentrations. Details of the pulse radiolysis set up are described elsewhere. 6,5 50 ns pulses of 7-MeV electrons from linear electron accelerator were used for irradiation and the pulse dose was about 15 Gy. Pulse dosimetry was performed by using 0.01 mol dm$^{-3}$ potassium thiocyanate solution, using a value of 21520 for (G.e) per 100 eV at 500 nm.

**Results and Discussion**

Reactions of OH radicals with 3-HBA were studied at pH 6.8. Time resolved absorption spectra of the transient species formed on pulse radiolysis of $N_2O$ saturated 1 x 10$^{-3}$ mol dm$^{-3}$ solutions of 3-HBA at pH 6.8 is given in Fig. 1. As can be seen from Fig. 1, the initial species has absorption maximum at 340 nm, which decayed by unimolecular process ($k_1 = 1.5 \times 10^5$ s$^{-1}$) to give a species having absorption maxima at 290 and two closely lying peaks at 390 and 410 nm. Rate constant for the reaction of OH radicals with 3-HBA was determined to be 2 x 10$^9$ dm$^3$ mol$^{-1}$ s$^{-1}$ by following the build up of transient absorption at 340 nm.

Absorption spectrum of the transient species formed in the reaction of $N_3$ radicals with 3-HBA was recorded in $N_2O$ saturated 3-HBA solutions, containing 0.02 mol dm$^{-3}$ NaN$_3$ and the same is given in Fig. 2.

Spectrum in Fig. 2 matches quite well with latter time window spectrum in Fig. 1. Thus it can be concluded that initial 3-HBA-OH adducts formed decay to give phenoxy radicals of 3-HBA. Some proportion of OH radicals can react with 3-HBA by H-abstraction from...
–CH₂OH group giving radicals containing –COH species which are reducing radicals. The yield of these radicals was determined by measuring the yield of methyl viologen radical cation which has strong absorption at 395 and 600 nm. It was estimated that 28% of the OH radicals react by H-abstraction from –CH₂OH groups.

At pH 6.8, experiments were carried out to investigate the dependence of decay rate of OH adducts on buffer concentrations. Equimolar concentrations of KH₂PO₄ and Na₂HPO₄ in the range 0.0005 mol dm⁻³ to 0.2 mol dm⁻³ were used. It was found that both the decay rate as well as rate of formation of phenoxyl radicals increases with buffer ion concentrations. Rate constant for the formation of phenoxyl radical varied from 4.2 x 10⁴ s⁻¹ at 0.001 M to 2.9 x 10⁵ s⁻¹ at 0.04 mol dm⁻³ buffer ion concentration. In Fig. 3, absorption traces obtained at 340 nm at different buffer ion concentrations are given. Traces showing the build-up of transient absorption at 410 nm due to phenoxyl radicals of 3-HBA are given in Fig. 4.

These traces clearly show that increase in the rate of formation with buffer is initially more pronounced and after certain concentration it reaches a plateau value. By making use of these traces, first order rate constant values were determined and the same are plotted against buffer ion concentration in Fig. 5.

At pH 1, in O₂ saturated solution reaction of OH radicals with 3-HBA radiolysis directly gave phenoxyl radicals. (Fig. 6). Spectra of the species formed was identical with that formed in the reaction of Cl₂ radicals with 3-HBA at pH 1. This showed that due to
higher reduction potential of OH radicals at pH 1 as compared to that at pH 6.8, it is able to oxidise 3-HBA quantitatively.

3-HBA has pKa 9.5 above which it exists in the deprotonated form. Reactions of OH radicals with 3-HBA were investigated at pH 10.5, with the aim to estimate the different pathways. Absorption spectrum of the transient species indicated, that there is direct formation of phenoxy radicals. Electron transfer to methyl viologen showed that nearly 28% of the OH radicals abstract H-atom from –CH2OH group. Based on these observations, following Scheme 1 has been assigned for the reaction of OH radicals with 3-HBA at pHs 1, 6.8 and 10.5.
Conclusions

Present study shows that hydroxyl radicals react with 3-hydroxybenzyl alcohol mainly by adduct formation reaction. Subsequent decay of the adduct to phenoxyl, depends very much on the phosphate buffer ion concentrations. Both with neutral and anionic forms of HBA, OH radical reaction give equal proportion of adduct as well as reducing radicals formed on H-atom abstraction from –CH₂OH group.

Acknowledgement

The authors thank Dr. S.K. Sarkar, Head, Radiation & Photochemistry Division and Dr. T. Mukherjee, Director Chemistry Group, BARC for their support to this work.

References


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