Characterization of the Transient Species Formed during the Pulse Radiolysis of 3-Hexyn-1-ol and 5-Hexyn-1-ol in Aqueous Solutions

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Reactions of the primary species of water radiolysis, viz. e_{aq}^-, H atoms, and $^•OH$ radicals, were studied with 3-hexyn-1-ol (3HX) and 5-hexyn-1-ol (5HX) using the pulse radiolysis technique. The rate constants for the reactions of e_{aq}^- with 3-hexyn-1-ol and 5-hexyn-1-ol were found to be 6.1×10^4 and 4.5×10^4 $m^3\ mol^{-1}\ s^{-1}$, respectively, whereas those for OH radical reactions with these compounds were 2.9×10^6 and 3.8×10^6 $m^3\ mol^{-1}\ s^{-1}$. The transient species formed in both cases were found to be good reductants. Oxide radical anion ($O^{•-}$) reacted with 3HX and 5HX with rate constants of 4.7×10^6 and 4.8×10^6 $m^3\ mol^{-1}\ s^{-1}$, respectively. The H atom reactions with hexyn-1-ols were found to give vinyl-type radicals which were reducing in nature. These radicals reacted with oxygen to give peroxyl radicals.

Introduction

Both H atoms and $^•OH$ radicals abstract hydrogen atoms predominantly[1] from the α-carbon atom in the case of short-chain aliphatic alcohols, while hydrated electrons are rather inert toward these alcohols. However, unsaturated alcohols, i.e., those having multiple bonds [e.g., allyl alcohol ($CH_2{=}CHCH_2OH$)[2] and propargyl alcohol ($CH{\equiv}CCH_2OH$)[3]] are more reactive toward e_{aq}^- as compared to saturated alcohols. In the case of allyl or propargyl alcohol, OH radicals or H atoms can also react by addition to the double bond or triple bond, as the case may be in addition to the abstraction reaction. Except for propargyl alcohol, there are no reports in the literature on radiation chemical studies of alcohols having a carbon−carbon triple bond. Two similar compounds are 3-hexyn-1-ol [$CH_3CH_2C{\equiv}CCH_2CH_2OH$] (3HX) and 5-hexyn-1-ol [$HC{\equiv}CCH_2CH_2CH_2CH_2OH$] (5HX). The transient species formed from these compounds are expected to exhibit properties similar to those exhibited by species formed from both acetylene and alcohols. The reactions of OH radicals with acetylene have already been reported.[4] However, in the case of hexyn-1-ols, OH radicals can react not only by addition to the triple bond but also by H abstraction. It has been reported[5] that vinyl radicals can be formed by the dissociative electron capture reaction of e_{aq}^- with vinyl halides as well as by H atom addition to acetylene and its derivatives. In the presence of oxygen, vinyl radicals are converted into vinyl peroxyl radicals which have measurable absorption in the UV as well as visible region.[5] Electron and H atom addition to the triple bond of hexyn-1-ols can also lead to the formation of vinyl-type radicals in the absence of oxygen and peroxyl radicals in the presence of oxygen. Hexyn-1-ols are also known to be good corrosion inhibitors,[6] which can be used along with dilute chemical decontamination formulations. These formulations are used for minimizing the radiation levels on the out-of-core surfaces in nuclear power plants by dissolving the radionuclides trapped in the oxide layer on the inner side of the metal pipings. The function of the corrosion inhibitor is to minimize the corrosion of the underlying metal[7] during this process. From this point of view, also, the radiation stability as well as radiation chemistry of these compounds will be of interest.

Experimental Section

e_{aq}^-, H atom, and $^•OH/O^-$ radials were generated in aqueous solutions by using 50-ns or 2-μs single-electron pulses from a 7-MeV linear electron accelerator (Ray Technologies). The details of the pulse radiolysis setup have been reported earlier.[8] The dose absorbed per pulse was about 15 Gy for the 50-ns pulse and 75 Gy for the 2-μs pulse and was determined by using a 10 mol/m^3 potassium thiocyanate dosimeter,[9] and a value of 2.23×10^{-4} m^2/J was used for $G\epsilon$ of the $(SCN)_2^{•-}$ radical at 500 nm.[9]

3-Hexyn-1-ol and 5-hexyn-1-ol from Aldrich were used as received since the carbonyl content in these compounds was found to be less than 0.2%. All the other chemicals were AnalaR reagents. Solutions were prepared in nanopure water (having a conductivity < 0.1 μS/cm) obtained from a Barnstead "nanopure water system". The pH's of the solutions were adjusted using phosphate and borate buffers as well as plain H_2SO_4 and NaOH. "Iolar"-grade gases, viz., N_2, O_2, or N_2O, from Indian Oxygen Ltd. were used for purging the solutions. For studying the reactions of e_{aq}^- and H atoms, *tert*-butyl alcohol was used as the $^•OH$ radical scavenger.[8] For studying the reactions of OH/O^- radicals, solutions were saturated with N_2O gas to convert e_{aq}^- into $^•OH$ radicals.

Results and Discussion

Hexyn-1-ols were found to be reactive toward all the primary species of water radiolysis, viz., e_{aq}^-, H atoms, and $^•OH$ radicals, and these reactions are discussed one by one below.

Reaction with e_{aq}^-. The rate constants for the reaction of e_{aq}^- with hexyn-1-ols were determined by following the first-order decay of hydrated electron absorbance at 720 nm. These were found to be 6.1×10^4 and 4.5×10^4 $m^3\ mol^{-1}\ s^{-1}$ for 3-hexyn-1-ol and 5-hexyn-1-ol, respectively. The reactivity of the hexyn-1-ols with e_{aq}^- can be attributed to the presence of a triple bond in these molecules, as in the case of propargyl alcohol.[3] The rate constant values for the e_{aq}^- reaction with these two hexyn-1-ols are somewhat lower than that for propargyl alcohol (2.1×10^5 $m^3\ mol^{-1}\ s^{-1}$), probably due to a longer intervening saturated hydrocarbon chain. Usually alcohols contain carbonyl compounds as impurities which may be partially responsible for the observed reactivity of hexyn-1-ols with e_{aq}^-. Estimation of carbonyl compounds in both 3HX and

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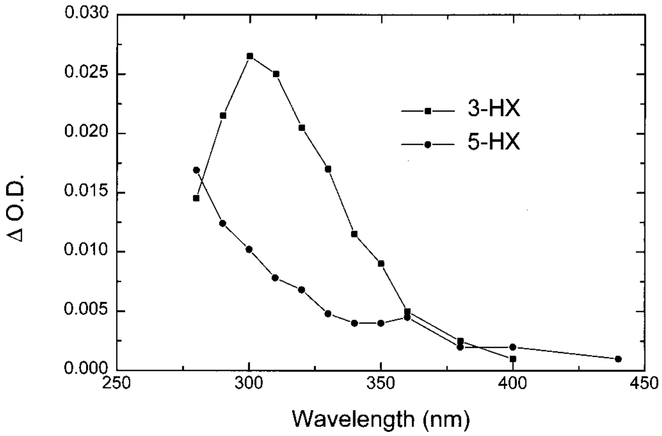
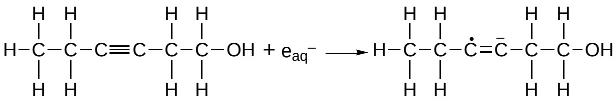
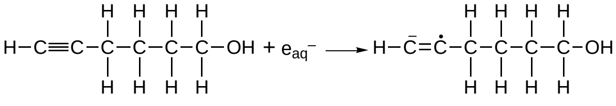


Figure 1. Transient spectra obtained in pulse-irradiated N_2-purged solutions at pH 7 with 10 mol/m^3 3HX and 5HX containing 10^3 mol/m^3 *tert*-butyl alcohol (dose: 80 Gy/pulse).

5HX by DNPH (dinitrophenylhydrazine) reagent showed that the concentration of these impurities was less than 0.2%. Thus, the contribution of carbonyl impurities toward the observed reactivity of hexyn-1-ols with e_{aq}^- is less than 10%, as carbonyl compounds usually react with e_{aq}^- with rate constants[10] in the range of 2 × 10^6 m^3 mol^{-1} s^{-1}. e_{aq}^- is known to react with acetylene with a rate constant of 2 × 10^4 m^3 mol^{-1} s^{-1}, and it has been suggested that the electron adduct is converted to a vinyl radical by protonation.[4] If we assume similar behavior in the case of e_{aq}^- addition to hexyn-1-ols, the vinyl-type radical should not have any absorption even in the UV region, as was found to be the case with H adducts of these compounds (see below). The absorption spectra of the transient species formed in 10 mol/m^3 N_2-purged solutions of these compounds containing 10^3 mol/m^3 *tert*-butyl alcohol as OH radical scavenger at pH 7 are given in Figure 1. These show an absorption peak around 300 nm in the case of semireduced species of 3HX, whereas in the case of 5HX, only a shoulder was observed in this wavelength region. The electron is expected to add to the triple bond in the molecule, and the probable reaction schemes are


$$\mathrm{H{-}CH_2{-}CH_2{-}C{\equiv}C{-}CH_2{-}CH_2{-}OH} + e_{aq}^- \longrightarrow \mathrm{H{-}CH_2{-}CH_2{-}\dot{C}{=}\bar{C}{-}CH_2{-}CH_2{-}OH} \quad (1)$$

3HX A


$$\mathrm{H{-}C{\equiv}C{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}OH} + e_{aq}^- \longrightarrow \mathrm{H{-}\bar{C}{=}\dot{C}{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}OH} \quad (2)$$

5HX B

The transient species formed decayed by second-order kinetics with a $2k/\epsilon l$ values of 5 × 10^5 s^{-1} (at λ = 300 nm) and 1.2 × 10^6 s^{-1} (at λ = 310 nm), respectively, in the case of 3HX and 5HX. Kinetic salt effects on the decay kinetics of these transient species showed that these are negatively charged compared to the case of acetylene, where the electron addition product gets protonated; in the case of both hexyn-1-ols, it remains negatively charged at pH 7 and above. We did the measurements down to pH 6 where it continued to show absorption. This is probably because of the presence of a hydroxyl group in these species. The spectral and kinetic properties of the transient species are listed in Table 1.

The transient species formed by e_{aq}^- reaction with both hexyn-1-ols were found to be strong reductants, and they transferred electrons to various electron acceptors, such as thionine, safranine T, methylviologen, etc. The rate constants for these reactions with different acceptor solutes were determined from the build-up kinetics of the absorbance of the semireduced acceptor species at their respective λ_{max} values and are listed in Table 2.

TABLE 1: Spectral and Kinetic Properties of the Transient Species Formed by the Reaction of e_{aq}^-, $^\bullet$OH, and $O^{\bullet-}$

species	pH	λ_{max}, nm	G, 0.1 μmol/J	$G\epsilon$, m^2/J	$k_{formation}$, m^3 mol^{-1} s^{-1}	$2k/\epsilon l$, s^{-1}
			With 3HX			
e_{aq}^-	7	300	2.8	1.90 × 10^{-4}	6.1 × 10^4	5.0 × 10^5
$^\bullet$OH	7	310	1.45	1.89 × 10^{-4}	2.9 × 10^6	3.0 × 10^6
$O^{\bullet-}$	13	330	1.55	2.17 × 10^{-4}	4.7 × 10^6	1.6 × 10^6
			With 5HX			
e_{aq}^-	7	310(s)[a]	2.8	8.12 × 10^{-5}	4.5 × 10^4	1.2 × 10^6
OH$^\bullet$	7	310(s)	1.45	8.7 × 10^{-5}	3.8 × 10^6	2.2 × 10^6
$O^{\bullet-}$	13	320	1.55	1.40 × 10^{-4}	4.8 × 10^6	1.0 × 10^6

[a] (S)—shoulder.

TABLE 2: Rate Constants for the Reactions of the Species Formed by e_{aq}^-, OH, and O^- Radical Reactions with 3HX and 5HX with Various Acceptor Solutes

solutes with	pH	rate const, m^3 mol^{-1} s^{-1}	
		3HX−e_{aq}^- adduct species	5HX−e_{aq}^- adduct species
MV^{2+}	7	2.3 × 10^6	2.7 × 10^6
TH$^+$	7	2.8 × 10^6	
SF$^+$	7	3.1 × 10^6	
AQS	7	1.2 × 10^6	
		3HX−OH rxn species	5HX−OH rxn species
MV^{2+}	7	3.3 × 10^6	2.2 × 10^6
Th$^+$	7	6.3 × 10^6	
SF$^+$	7	2.3 × 10^6	
		3HX−O^- rxn species	5HX−O^- rxn species
MV^{2+}	13	7.3 × 10^6	7.5 × 10^6

$(CH_3)_2COH$ as well as $CO_2^{\bullet-}$ radicals could not reduce these substrates at pH 7. This indicates that the one-electron reduction potentials of the hexyn-1-ols are more negative than −1.9 V vs NHE,[11] the value for $CO_2^{\bullet-}$ radicals.

Reaction with H Atoms. In the case of H atom reaction with hexyn-1-ols, no light-absorbing transient species were observed in the wavelength region of 280−850 nm. The rate constants for the reaction of H atoms with 3HX and 5HX at pH 2 were determined by the competition kinetics method using thionine as a reference solute (rate constant for the thionine−H atom reaction is 9 × 10^6 m^3 mol^{-1} s^{-1}).[8] The plots of OD$_{max}$/OD vs [hexyn-1-ol]/[thionine] are shown in Figure 2. From these plots, the rate constant values were determined to be 3.2 × 10^6 and 2.3 × 10^6 m^3 mol^{-1} s^{-1} for 3HX and 5HX, respectively. High rate constant values suggest that H atoms react by addition to the triple bond, giving vinyl-type radicals. H atoms are known to react with acetylene[5] by addition to give vinyl radicals with a rate constant of 2.2 × 10^6 m^3 mol^{-1} s^{-1}. Such radicals in the case of allyl alcohol are reported to have very weak absorption in the UV region.[10] The product species formed by H atom reaction with 3HX and 5HX were found to transfer electrons to methylviologen. The rate constants for these reactions were determined to be 3 × 10^5 and 5 × 10^5 m^3 mol^{-1} s^{-1}, respectively. H atom reactions with hexyn-1-ols were also studied at pH 5.8 using 10^3 mol/m^3 phosphate buffer to convert e_{aq}^- to H atoms. In this case, also, the transient species exhibited weak absorption below 280 nm. Thus, even at this pH, vinyl radicals do not deprotonate to give a species similar to that formed by e_{aq}^- reactions.

Formation of Peroxyl Radicals. In the presence of oxygen, the species formed by H atom reaction with hexyn-1-ols were

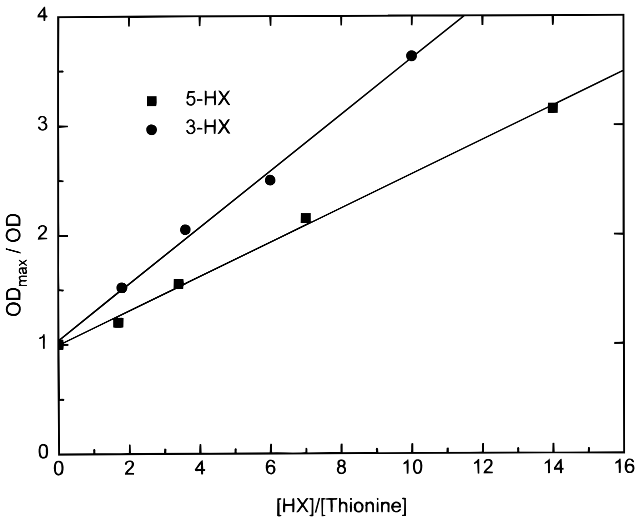


Figure 2. Plot of OD_{max}/OD vs [3HX]/[thionine] and OD_{max}/OD vs [5HX]/[thionine] in N_2-purged 0.1 mol/m^3 thionine solutions containing 10^3 mol/m^3 *tert*-butyl alcohol at pH 2 with different concentrations of hexyn-1-ols.

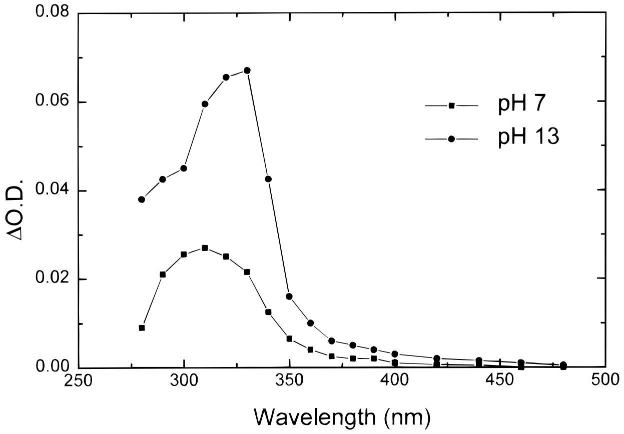


Figure 3. Transient spectra obtained in pulse-irradiated N_2O-saturated 1 mol/m^3 3HX (a) at pH 7 and (b) at pH 13 (dose: 80 Gy/pulse).

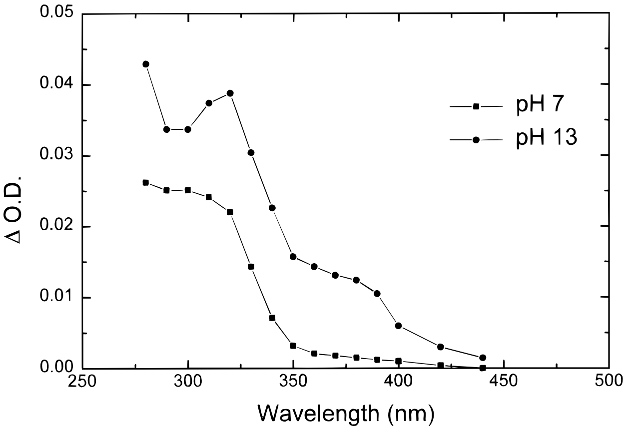


Figure 4. Transient spectra obtained in pulse-irradiated N_2O-saturated 1 mol/m^3 5HX (a) at pH 7 and (b) at pH 13 (dose: 80 Gy/pulse).

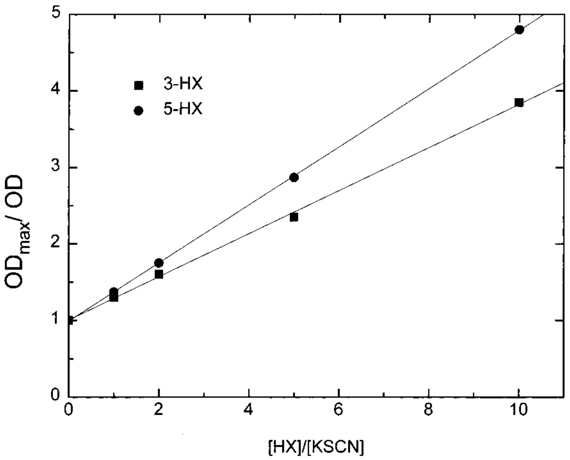


Figure 5. Plot of OD_{max}/OD vs [3HX]/[KSCN] and plot of OD_{max}/OD vs [5HX]/[KSCN] in N_2O-saturated 1 mol/m^3 KSCN solution at pH 7 with different concentrations of hexyn-1-ols.

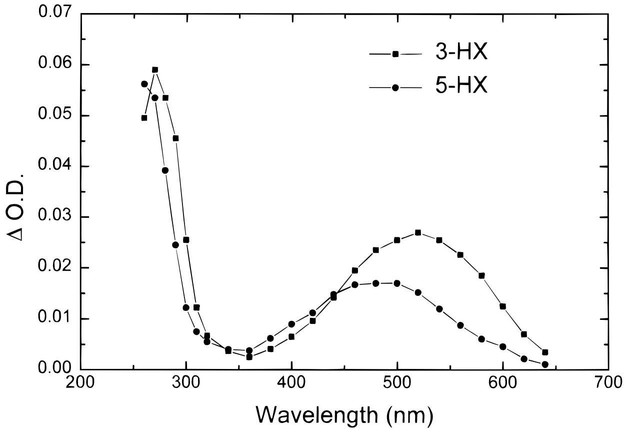
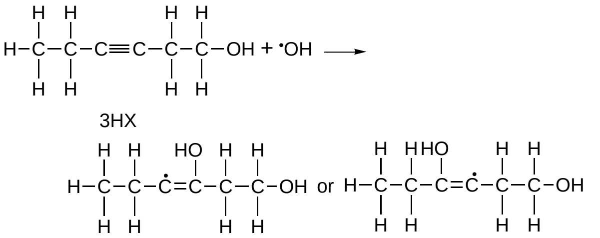


Figure 6. Transient spectra obtained in pulse-irradiated O_2-purged solutions of 50 mol/m^3 3HX and 5HX containing 10^3 mol/m^3 *tert*-butyl alcohol (dose: 80 Gy/pulse).

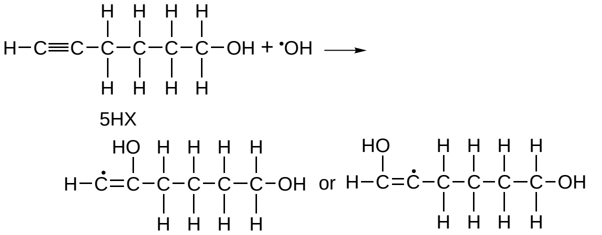
found to give peroxyl radicals. The transient absorption spectra monitored in acidic solutions of hexyn-1-ols at pH 1 (containing 10^3 mol/m^3 *tert*-butyl alcohol) are given in Figure 6. The overall shapes of the spectra compare very well with those of the vinyl peroxyl radicals reported in the literature.[5] The peroxyl radicals formed from 3HX have absorption in the visible region with a peak at 520 nm, whereas the peroxyl radicals formed from 5HX have a broad band at 460−500 nm. The rate constants for the reaction of oxygen with H atom adducts of hexyn-1-ols were determined by following the buildup of the transient absorption signal at the respective absorption maxima and were found to be 4×10^6 and 3.2×10^6 m^3 mol^{-1} s^{-1} for 3HX and 5HX, respectively. These peroxyl radicals were found to decay by second-order kinetics in the absence of other additives. They could bring about oxidation of thionine, and the rate constants for the reaction as measured by following the bleaching of thionine absorption at 600 nm were of the order of 5×10^5 m^3 mol^{-1} s^{-1}. It may be mentioned here that there is no reaction between thionine and *tert*-ButOO$^\bullet$ or HO_2 radicals.[8] These results are in agreement with those reported earlier,[5] where vinyl peroxyl radicals were found to be good oxidants.

Reaction with $^\bullet$OH/O$^-$ Radicals. The absorption spectra of the transient species formed by the reaction of $^\bullet$OH radicals in 0.1 mol/m^3 N_2O-saturated solutions of 3HX and 5HX at pH 7 are given in Figures 3 and 4, respectively. These show absorption bands with λ_{max} at 310 nm for 3HX and a shoulder at around 290 nm for 5HX with a maximum at a shorter wavelength. These absorptions could not be used for estimating the rate constants as the extinction coefficient values were very low. Hence, the rate constants for the OH radical reactions were determined by the competition kinetics method using thiocyanate[12] as the reference solute ($k_{OH+SCN^-} = 1.1 \times 10^7$ m^3 mol^{-1} s^{-1}). The plots of OD_{max}/OD vs [hexyn-1-ol]/[thiocyanate] are shown in Figure 5, from which the rate constant values were calculated to be 2.9×10^6 and 3.8×10^6 m^3 mol^{-1} s^{-1} for 3HX and 5HX, respectively. $^\bullet$OH radicals react with alcohols such as methanol, ethanol, etc., with rate constants of the order of 10^6 m^3 mol^{-1} s^{-1}. The species so produced are usually reducing in nature. The transient species formed by $^{\bullet}$OH radical reaction with hexyn-1-ols were also found to be strong reductants and could reduce methylviologen ($E^{\circ 1} = -0.45$V vs NHE).[13] Hence, it can be assumed that in this case, also, $^{\bullet}$OH radicals react by H abstraction. It is possible that a portion of $^{\bullet}$OH radicals may react by addition to the triple bond, but the species so produced may not have significant absorption in the wavelength region 280−800 nm, as in the case of the H adduct.

The decay of the transient species formed by OH radical reaction with hexyn-1-ols followed second-order kinetics. Kinetic salt effect experiments indicated that the transient species are neutral in nature, as their decay was unaffected by changing the ionic strength. The possible reaction schemes are given below:



(3)



(4)

In the case of alcohols of short-chain hydrocarbons, it has been observed that H abstraction from the α-carbon atom is the most predominant. This was confirmed by the electron transfer from the intermediates formed after H abstraction either to nitrobenzene[14] or to hexacyanoferrate(III).[15] Since the transient species formed by $^{\bullet}$OH radical reaction with 3HX and 5HX could reduce methylviologen (which has a reduction potential of −0.45 V vs NHE),[13] these species are strong reductants. The yield of MV^+ radical cation in the electron-transfer reactions indicated that in the case of 3HX, about 25% of the OH radicals are reacting by H abstraction from the α-carbon atom, while the rest are reacting either by addition to the triple bond or H abstraction from other sites. At higher pH values (pH > 12), $^{\bullet}$OH radicals are converted to $O^{\bullet -}$ radical anions,[16] which react predominantly by H abstraction. In the case of O^- reaction, also, only about 50% of the radicals reacted to give MV^+ radical cation, thus showing that about 50% of the O^- are abstracting H atoms from the α-carbon atom and the rest are reacting at other sites, forming nonreducing species. Therefore, the intermediate species which have absorption in the wavelength region 250−800 nm are inferred to be formed by H abstraction from the α-carbon atom. The transient spectra obtained by O^- radical reaction with 3HX and 5HX at pH 13 are shown in Figures 3 and 4, respectively, along with those obtained by OH radical reaction at pH 7. The changes in the spectra at alkaline pH's can be attributed to depronoration of the transient species.

The rate constants for the reactions of O^- at pH 13 as determined by following the buildup of the absorption of the transient species at 330 nm for both 3HX and 5HX are given in Table 1. The decay of the transient species followed second-order kinetics in both cases. The rate constants for the reactions of these transient species with methylviologen were determined by following the formation of MV^+ radical cation at 600 nm, and the values are given in Table 2.

As suggested above, about 50% of the O^- radical anions abstract H atom from the α-carbon atom of hexyn-1-ols, giving transient species which are the deprotonated forms of the radicals formed by H-abstraction reactions of OH radicals with hexyn-1-ols. The deprotonated forms of the alcohol radicals are stronger reductants as compared to the protonated species; e.g., $(CH_3)_2CO^-$ is a stronger reducing agent than $(CH_3)_2COH$;[11] hence, the deprotonated forms of the product species formed by O^- reaction at pH 13 should also be stronger reductants as compared to those formed by OH radical reaction at pH 7. This is borne out by the results of the experiments with methylviologen shown in Table 2, where the deprotonated forms of the transient species obtained by O^- reaction with 3HX and 5HX, at pH 13, react with MV^{2+} at a much faster rate than the protonated form.

Conclusion

The behavior of hexyn-1-ols toward primary species of water radiolysis was found to be different as compared to those of saturated alcohols. While the reactivity with OH radicals did not change, it was enhanced in the case of e_{aq}^- reaction. e_{aq}^- reacts by addition to the triple bond, whereas OH radicals react mainly by addition to the triple bond and H abstraction from the α-carbon atom. The transient species obtained by the reactions of e_{aq}^- and OH radicals were found to be strong reductants. The transient species formed in the case of 3HX have absorption bands at longer wavelengths as compared to those obtained in the case of 5HX. H atom reaction with hexyn-1-ols leads to the formation of vinyl-type radicals which react with oxygen to give peroxyl radicals. These peroxyl radicals were found to be oxidizing in nature.

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