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Transformation of OH-adduct of 1-chloro-4-iodobutane into intra-molecular radical cation in neutral aqueous solution

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Abstract

The iodine centered OH-adduct formed on reaction of $^{\cdot}$OH radicals with 1-chloro-4-iodobutane in neutral aqueous solution transforms ($k = 5.4 \times 10^{5}\ \mathrm{s}^{-1}$) to an intra-molecular radical cation $(\underbrace{-\overset{+}{\mathrm{I} \therefore \mathrm{Cl}}-}_{})$. The unfavorable structural conformation of solute radical cation generated on reaction of $^{\cdot}$OH radicals with 1-chloro-5-iodopentane does not allow the transformation of OH-adduct into an intra-molecular radical and instead a dimer radical cation $(-\overset{+}{\mathrm{I} \therefore \mathrm{Cl}}-)$ is formed.

1. Introduction

Hydroxyl radicals are known to react with alkyl iodides in neutral aqueous solution and form a 2-center 3-electron bonded OH-adduct which has absorption bands at 310 and 350 nm [1–3]. Dimer radical cations formed in acidic solutions have absorption bands in the 410–450 nm region. On the other hand, the yield and the life-time of the intra-molecular radical cation generated from 1,*n*-diiodoalkanes are known to depend strongly on the chain length between two iodine atoms [4]. In the case of alkyl chlorides, neither OH-adduct nor $^{\cdot}$OH radical induced oxidation is observed. Radical cations derived from organic compounds containing $2\sigma/1\sigma^{*}$ three-electrons have been the subject of many experimental and theoretical investigations [5–9]. These bonds can be formed on interaction of an oxidized hetero atom such as S, N, P, I, Br with the free electron pair of a second hetero atom both by inter- and intra-molecular association. $2\sigma/1\sigma^{*}$ bonding between two dissimilar hetero atoms is possible if the difference in the electronegativity is small and stabilization is provided by a favorable structural conformation for sufficient p-orbital overlap [10–12]. Generally, the formation of these radical cations is very fast and is complete within a few hundreds of nanoseconds. The observation of a 3-electron bonded OH-adduct and its transformation into a solute radical cation in neutral solutions has not been reported in the literature so far. The transformation of OH-adduct does not take place in neutral solutions while it is too fast to be detected in acidic solutions. The only example of OH-adduct transforming into a solute radical cation has been reported at pH = 3.7 [13]. This conversion was fast and was complete within 600 ns [13].

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If the difference in the electronegativity of two hetero atoms is comparatively large and stabilization of the solute radical cation is provided by a favorable structural conformation, the transformation of OH-adduct to a solute radical cation could be a too slow process to be observed in microsecond time scale. Given the large difference in the electronegativities of iodine and chlorine (0.62 eV) and the possibility of formation of a stable six-membered ring configuration for the solute radical cation of 1-chloro-4-iodobutane, the transformation of OH-adduct to solute radical cation in neutral solutions might be slow enough and detectable in microsecond time scale. With this objective, 1-chloro-*n*-iodoalkanes were synthesized and the results of pulse radiolysis studies on their aqueous solutions are reported here.

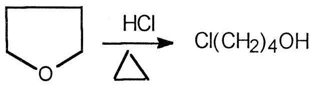
2. Experimental

2.1. Synthesis of 1-chloro-n-iodoalkanes

1-chloro-4-iodobutane (CIB) and 1-chloro-5-iodopentane (CIP) were synthesized and purified in the laboratory just before use and the detailed procedure is mentioned below.

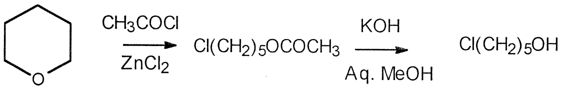
2.2. Preparation of 4-chlorobutanol

HCl (gas) was bubbled slowly through refluxing tetra hydrofuran (50.7 g, 0.79 mol). The temperature of the reaction mixture rose gradually during 4 h. It was heated for further 2 h when the temperature became steady. The resultant brown liquid was evacuated at 50 mm pressure. The resultant mixture was then distilled to get 4-chlorobutanol (45 g, b.p. 75–78°C/6 mm) [14].



2.3. Preparation of 5-chloropentanol

Dry tetrahydropyran (30.1 g, 0.35 mol) was added to a mixture of acetyl chloride (23.6 g, 3 mol) and dry $ZnCl_2$ (5 g). After the initial reaction subsided, the mixture was heated at 80°C for 2 h. It was poured in benzene and the benzene layer washed carefully with water, 10% aqueous Na_2CO_3, water and brine. After drying, the residue was distilled to get 5-chloropentyl acetate (33.5 g, b.p. 95–98°C/9 mm). It (33.5 g, 0.2 mol) was then mixed with 6% aqueous methanolic KOH and warmed to 60°C. After 2 h, the mixture was concentrated and the residue in ether layer was washed with water and brine and dried. Removal of the solvent gave 5-chloropentanol (13.5 g, b.p. 80–81°C/8 mm) [15].



2.4. Preparation of 1-chloro-n-iodoalkanes

To a cooled (0°C) and stirred mixture of the chloroalkanol (0.01 mol) and NaI (0.011 mol) in acetonitrile (20 ml), under Ar, was slowly injected TMSCl (0.011 mol). The mixture was brought to room temperature and stirred for 12 h. It was poured in ice–water, extracted with pentane. The pentane layer was washed with aqueous $Na_2S_2O_3$, water and brine and dried. The concentration of the extract followed by repeated (4–6 times) column chromatography of the residue over silica gel (pentane as eluent) gave the respective pure 1-chloro-*n*-iodoalkanes.

The purity of the products was checked with NMR (in $CDCl_3$, Bruker AC-200, 200 MHz) and IR (Perkin-Elmer IR spectrophotometer model 837).

$$\mathrm{Cl(CH_2)_nOH} \xrightarrow[\mathrm{CH_3CN}]{\mathrm{NaI/TMSCl}} \mathrm{Cl(CH_2)_nI}$$

n=4; CIB
n=5; CIP

2.5. Pulse radiolysis studies

The pulse radiolysis studies were performed with high-energy (7 MeV) electron pulses (50 ns) obtained from a linear electron accelerator [16]. The dose delivered per pulse was determined by using an aerated aqueous solution of KSCN and it was close to 15 Gy (1 Gy = 1 J kg^{-1}). The solutions were prepared in deionized 'nano-pure' water containing 1×10^{-3} mol dm^{-3} phosphate buffer. All other details about sample preparation and kinetic analysis are available elsewhere [11,12].

3. Results and discussion

The transient optical absorption spectrum obtained on pulse radiolysis of N_2O-saturated neutral aqueous solution of CIB exhibited bands with λ_{max} = 315 and 360 nm (Fig. 1a). These bands were not observed in the presence of *t*-butanol (0.3 mol dm^{-3}), an efficient $^{\cdot}OH$ radical and weak $^{\cdot}H$ atom scavenger, indicating that the contribution of reaction of $^{\cdot}H$ atom with the solute was negligible. Thus, the absorption spectrum (Fig. 1a) was due to the reaction of $^{\cdot}OH$ radicals with CIB. The pseudo-first-order rate constant (k_{obs}) for the reaction of $^{\cdot}OH$ radicals with CIB, determined on monitoring the growth of the transient absorption at 315 nm, was found to increase linearly with solute concentration, $(0.3–1.6) \times 10^{-3}$ mol dm^{-3}. The bimolecular rate constant, determined from the linear plot of k_{obs} vs. solute concentration gave a value of 4.7×10^9 dm^3 mol^{-1} s^{-1}. The initial portion of the transient absorption at 315 and 360 nm decayed by first-order kinetics with $k = 5.2 \times 10^5$ s^{-1} (inset of Fig. 1). Simultaneously, the transient absorption at 420 nm was observed to grow by first-order kinetics with $k = 5.4 \times 10^5$ s^{-1} (inset of Fig. 1), matching with the decay at 315 nm.

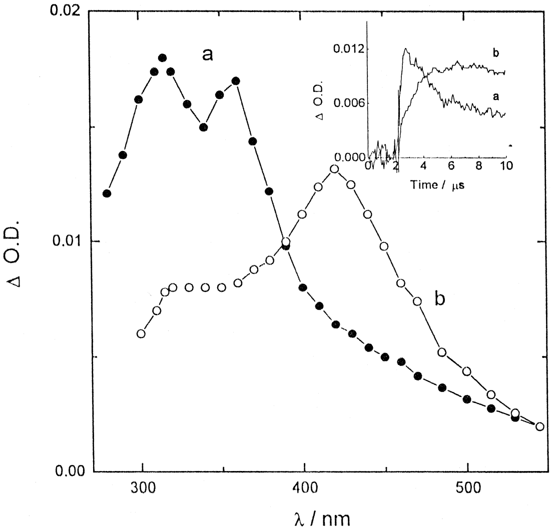


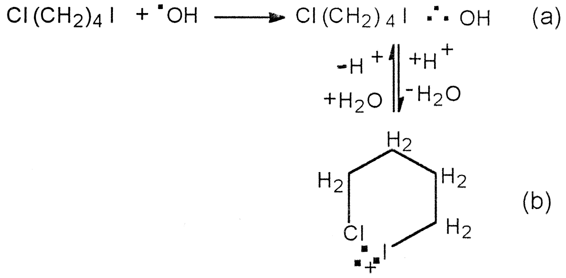
Fig. 1. Transient absorption spectra obtained on pulse radiolysis of N_2O-saturated aqueous solution of CIB (1.6×10^{-3} mol dm^{-3}, pH = 6.5) in 1×10^{-3} mol dm^{-3} phosphate buffer 1 (a) and 6 µs after a 50 ns electron pulse (b). Inset show absorption–time profiles at 315 (a) and 420 nm (b). Dose per pulse = 1×10^{17} eV g^{-1}.

Time-resolved studies showed the formation of transient absorption band at 420 nm (Fig. 1b). The latter portion of the transient absorption at 315 and 420 nm decayed by first-order kinetics with $k = (3 \pm 1) \times 10^4$ s^{-1}. These studies also revealed that the transient absorption bands at 315 and 360 nm (Fig. 1a) were due to a transient species which on decay gave another transient species absorbing at 420 nm (Fig. 1b). The transient absorption at 315 nm remained independent of solute concentration $(0.4–2) \times 10^{-3}$ mol dm^{-3}, suggesting that the entire amount of $^{\cdot}OH$ radicals have reacted with the solute and the transient species was not a dimer. Under these conditions, the concentration of the transient species could be taken equal to the concentration of $^{\cdot}OH$ radicals and the molar absorptivity at 315 nm was determined to be 1.9×10^3 dm^3 mol^{-1} cm^{-1}.

Pulse radiolysis of N_2O-saturated aqueous solution of 1-iodobutane showed the formation of transient absorption bands at 315 and 360 nm without any transformation into any other transient species. The absorption bands were assigned to the OH-adduct. Pulse radiolysis of N_2O-saturated aqueous solution of 1-chlorobutane did not show these transient absorption bands. Therefore, the absorption bands observed on pulse radiolysis of N_2O-saturated aqueous solution of CIB are assigned to iodine centered OH-adduct [Scheme 1, (a)]. It is proposed that this OH-adduct undergoes transformation to an intra-molecular radical cation which is stabilized due to the formation of a six-membered ring configuration [Scheme 1, (b)].

3.1. *Evidences in support of intra-molecular radical cation*

(a) If the proposed reaction mechanism is operative, then OH-adduct should not undergo any trans-



Scheme 1.

formation at higher pH. In addition, at lower pH, the transformation should be very fast and formation of only intra-molecular radical cation absorbing at 420 nm is expected.

The transient absorption spectrum obtained on pulse radiolysis N_2O-saturated aqueous solution of CIB at pH = 9.8 exhibited absorption bands at 310 and 340 nm (Fig. 2a), without any growth at 420 nm (inset of Fig. 2, c). The transient absorption spectrum at pH = 9.8 is blue-shifted as compared to the spectrum obtained at neutral pH. Although the exact reason for this shift is not known at present, it may not be due to the hydrolysis of the solute as I^- formed on hydrolysis would give an absorption band at 385 nm. The nature of the transient species is not expected to be different as the time-resolved studies at neutral and acidic solutions have shown the transient absorption band at 420 nm. The absorbance and growth rate of the transient absorption band at 420 nm increased at lower pH, indicating that the transformation of OH-adduct at lower pH is very fast and is in accordance with the proposed reaction mechanism (Scheme 1). The pseudo-first-order rate constant (k_{obs}) determined by monitoring the growth of the transient absorption at 420 nm as a function of H^+ concentration gave a bimolecular rate constant of 2.9×10^8 dm^3 mol^{-1} s^{-1}. This value is two orders of magnitude less than that observed for the reaction of $^{\bullet}OH$ radicals with methyl thiomethylacetate [13]. This explains the reason for observing the transformation of OH-adduct of CIB into solute radical cation. Variation of normalized absorbance [ΔO.D/G(OH)] at 420 nm gave an approximate value of inflection point at pH ≈ 4 (inset of Fig. 2). This should be due to the transformation of OH-adduct into solute radical cation (Scheme 1), as the ground state absorption spectrum of CIB did not show any variation with pH in this region. At pH = 2, the transient absorption spectrum showed a band at 420 nm (Fig. 2b). The absorbance of this band remained independent of solute concentration, suggesting it to be due to a monomeric species. Simple iodine centered monomer radical cations of alkyl iodides absorb at 310 nm [3]. Therefore, the transient absorption (Fig. 2b) is not due to a simple iodine centered radical cation. It could be due to a intra-molecular radical cation formed on p-orbital overlap of oxidized iodine with Cl (Scheme 1). Intra-molecular radical cation formed on p-orbital overlap between two halogens are reported to absorb in this region [4,11,12,17]. Under these conditions, the molar absorptivity of the transient band at 420 nm was determined to be 5.5×10^3 dm^3 mol^{-1} cm^{-1}. The bimolecular rate constant for the reaction of $^{\bullet}OH$ with CIB at pH = 2, determined by formation kinetic studies at 420 nm, gave a value of 3.5×10^9 dm^3 mol^{-1} s^{-1}. The band at 420 nm decayed by first-order kinetics with $k = 2 \times 10^4$ s^{-1} (Table 1).

The comparison of interhalogen intra-molecular radical cations revealed that: (1) the site of $^{\bullet}OH$

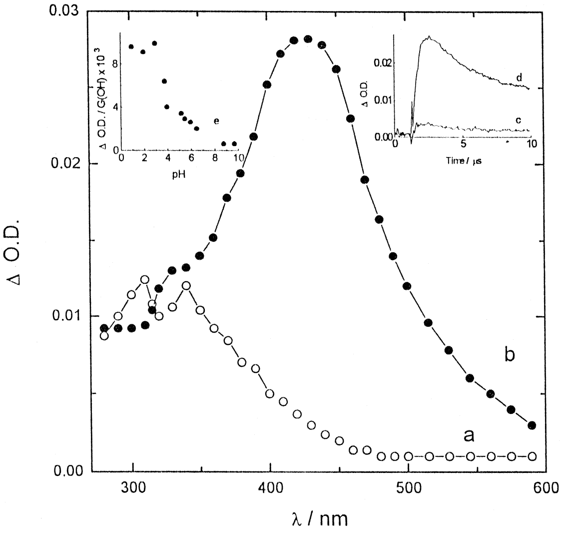


Fig. 2. Transient absorption spectra obtained on pulse radiolysis of N_2O-saturated solution of CIB (1.6×10^{-3} mol dm^{-3}) in 1×10^{-3} mol dm^{-3} phosphate buffer at pH = 9.8 (a) and pH = 2 (b). Inset show absorption time profiles at 420 nm at pH = 9.8 (c) and pH = 2 (d) and variation of normalized absorbance (420 nm) as a function of pH (e).

Table 1
Kinetic parameters for the transient species formed on reaction of $^{\bullet}$OH radicals with CIB and CIP

Solute	pH	λ_{max}	k_f (dm^3 mol^{-1} s^{-1})	ε (dm^3 mol^{-1} cm^{-1})	k_d (s^{-1})
CIB	7	315, 360	4.7×10^9	$1.9 \times 10^{3\,a}$	5.2×10^5
		420	–	–	3.1×10^4
CIB	2	420	3.5×10^9	$5.5 \times 10^{3\,b}$	2.1×10^4
CIP	7	310, 350	3.8×10^9	–	6.5×10^5
CIP	1	430	2.1×10^9	–	6.3×10^4

[a] 315 nm.
[b] 420 nm.

radical attack is the halogen having lower electronegativity and (2) the concentration of H^+ required for acid-catalyzed dehydration was observed to depend on the ionization potential of the alkyl halide. Alkyl bromides having an ionization potential in the 10.1–10.3 eV region required ≥ 3 mol dm^{-3} $HClO_4$ for the formation of radical cations as compared to 10^{-2} mol dm^{-3} required in the case of alkyl iodides whose ionization potential is in the range of 9.1–9.4 eV. The stability of radical cation is also observed to depend on the electronegativity (E_N) of halogen. The iodine centered ($E_N = 2.21$ eV) intra-molecular radical cation of 1-iodo-4-chlorobutane and 1-bromo-4-iodobutane has a half-life of 34 and 20 μs, respectively, whereas the bromine centered ($E_N = 2.74$ eV) intra-molecular radical cation of 1-bromo-4-chlorobutane has a half-life of 9 μs. The presence of halogen having higher electronegativity has lowered the life time of the intra-molecular radical cation. Chlorine ($E_N = 2.83$ eV) centered intra-molecular radical cations of alkyl chlorides could not be experimentally observed. The difference in the electronegativity of two halogens along with the favorable structure of the interhalogen intra-molecular radical cation seems to play an important role in the stabilization of the intra-molecular radical cation.

(b) The evidence for the assignment of the transient absorption spectrum obtained on pulse radiolysis of CIB to intra-molecular radical cation came from the pulse radiolysis studies on CIP. The solute radical cation of CIP would form a seven-membered ring configuration which is expected to be very unstable. Pulse radiolysis of N_2O-saturated neutral aqueous solution of CIP exhibited absorption bands at 310 and 350 nm (Fig. 3a) without any transformation. The bands are slightly blue-shifted as compared to those of OH-adduct of CIB at neutral pH. In acidic solutions, the transient absorption spectrum showed a band at 430 nm (Fig. 3b). The absorbance at 430 nm was found to depend strongly on solute concentration (inset of Fig. 3), suggesting the 430 nm band to be due to a dimer radical cation. In absence of a stable seven-membered ring configuration in the case of CIP, inter-molecular dimer radical cation was formed. The absence of transformation of

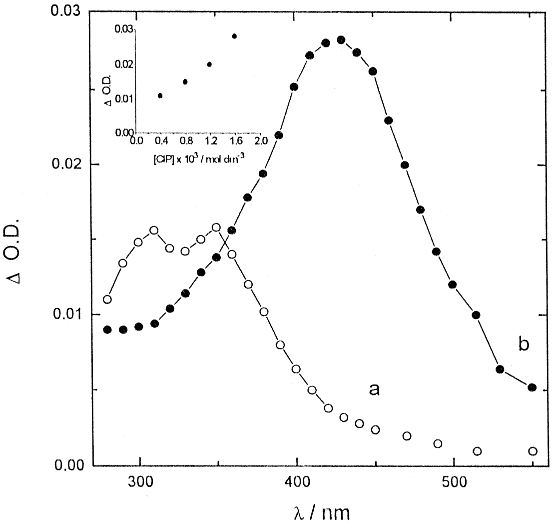


Fig. 3. Transient absorption spectra obtained on pulse radiolysis of N_2O-saturated aqueous solution of CIP (1.4×10^{-3} mol dm^{-3}) at pH = 7 (a) and pH = 1 (b) in 1×10^{-3} mol dm^{-3} phosphate buffer. Inset shows variation of absorbance at 430 nm as a function of solute concentration.

OH-adduct to solute radical cation at neutral solution and formation of a dimer radical cation supported the assignment of intra-molecular radical cation for CIB. In the case of CIB, the formation of a stable six-membered ring configuration has favored the transformation of its OH-adduct to intra-molecular radical cation. In contrast, with CIP, the unstable seven-membered ring configuration did not favor the conversion of OH-adduct into an intra-molecular radical cation but led to a dimer radical cation in acidic solutions.

(c) The evidence in support of the assignment of the transient absorption band to radical cation was also obtained from the electron transfer studies. $Cl_2^{\cdot-}$ is a strong one-electron oxidant with oxidation potential = 2.06 V. The decay of the transient band of $Cl_2^{\cdot-}$, formed on pulse radiolysis of aerated acidic aqueous solution of Cl^- (2×10^{-2} mol dm^{-3}, pH = 1, $\lambda = 345$ nm), was observed to decay faster on addition of low concentration of CIB $(1\text{–}3) \times 10^{-4}$ mol dm^{-3} and the bimolecular rate constant was determined to be 1.6×10^8 dm^3 mol^{-1} s^{-1}. Time-resolved studies have also shown increased absorption in the 400–450 nm region. Thus it supported electron transfer from CIB to $Cl_2^{\cdot-}$ [reaction (1)] and assignment of the transient absorption band to the solute radical cation. Therefore, the oxidation potential of CIB/CIB$^{\cdot+}$ couple should be less than that of the $Cl_2^{\cdot-}/2Cl^-$ couple ($E^o = 2.06$ V).

$$Cl_2^{\cdot-} + CIB \rightarrow CIB^{\cdot+} + 2Cl^- . \qquad (1)$$

However, earlier pulse radiolysis studies [11] had shown that $Cl_2^{\cdot-}$ is unreactive towards 1-bromo-2-chloroethane, which may be due to the presence of bromine having a higher electronegativity (2.74 eV) as compared to iodine (2.21 eV). The presence of halogen having higher electronegativity must have increased the oxidation potential. Fluorine in alkyl iodides has also increased the oxidation potential of alkyl iodides and one-electron oxidation of fluorinated alkyl iodides becomes difficult as compared to alkyl iodides [3,17].

The decay of the transient absorption band of CIB$^{\cdot+}$, formed on pulse radiolysis of N_2O-saturated acidic aqueous solution of CIB (4×10^{-3} mol dm^{-3}, pH = 1, $\lambda = 420$ nm) was accelerated on addition of low concentration of I^- (2.5×10^{-5} mol dm^{-3}), indicating electron transfer from I^- to CIB$^{\cdot+}$ [reaction (2)].

$$CIB^{\cdot+} + I^-/Br^- \rightarrow CIB + I^{\cdot}/Br^{\cdot} . \qquad (2)$$

The bimolecular rate constant was determined to be 4.8×10^9 dm^3 mol^{-1} s^{-1}. Similarly, the electron transfer was also observed from Br^- to CIB$^{\cdot+}$ [reaction (2)] with a bimolecular rate constant of 3×10^9 dm^3 mol^{-1} s^{-1}. The electron transfer is possible from Br^- to CIB$^{\cdot+}$, therefore, the oxidation potential of CIB/CIB$^{\cdot+}$ couple should be more than that of $Br_2^{\cdot-}/2\,Br^-$ couple ($E^o = 1.62$ V).

All these studies suggested that the transient species formed on reaction of $^{\cdot}OH$ radicals with CIB is cationic in nature and the oxidation potential of CIB/CIB$^{\cdot+}$ couple is between 1.6 and 2.1 V.

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