Structure–Reactivity Studies on the Nature of Transients Formed on Reaction of ·OH Radicals with Chloroiodoalkanes in Aqueous Solution

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The transient optical absorption bands (λ_{max} = 315 and 345 nm) formed on reaction of ·OH radicals with 1-chloro-3-iodopropane in N_2O-saturated neutral aqueous solutions have been assigned to an OH-adduct formed between iodine atom and ·OH radicals ($t_{\frac{1}{2}}$ = 1.5 µs, ε_{350} = 2.46 × 10^3 dm^3 mol^{-1} cm^{-1}). In acidic solutions, iodine-centred radical cations (λ_{max} = 345 nm, $t_{\frac{1}{2}}$ = 4.0 µs, ε_{345} = 2.41 × 10^3 dm^3 mol^{-1} cm^{-1}) are formed at low solute concentrations and dimer radical cations (λ_{max} = 430 nm, $t_{\frac{1}{2}}$ = 16.0µs, ε_{430} = 6.7 × 10^3 dm^3 mol^{-1} cm^{-1}) at high solute concentrations. In chloroiodomethane, the ·OH radicals do not seem to form OH-adducts in neutral aqueous solutions. In acidic solutions, intramolecular radical cation (λ_{max} = 430 nm, $t_{\frac{1}{2}}$ = 8.0 µs, ε_{430} = 2.63 × 10^3 dm^3 mol^{-1} cm^{-1}) with oxidized iodine and chlorine is observed. The intermolecular dimer radical cations are formed at high solute concentration (λ_{max} = 500 nm).

In addition to the most studied process of dissociative electron capture by alkyl halides, a variety of other reactions are now established which include the formation of charge-transfer complexes, halogeno radicals and radical cations.[1–9] The nature of transients formed on γ-radiolysis and photolysis of alkyl halides in hydrocarbon glasses at low temperature have been assessed from the effect of known hole and electron scavengers.[9–13] The radical cations of alkyl halides have been inferred to be formed on charge transfer from solvent to solute.[9–13] Experimental evidence for the formation of radical cations has come from time-resolved studies using pulse radiolysis,[5,6,13–16] EPR,[7] and mass spectrometric investigations.[17]

Although the ·OH radicals are strong oxidizing species they have been inferred to react with alkyl iodides to form OH-adducts.[2,3] Recently, radical cations have been identified as the transient intermediates formed on reaction of ·OH radicals with iodo compounds in aqueous solutions.[5,6,18,19] The radical cations of organic molecules containing hetero functions such as sulfur, nitrogen, oxygen, phosphorous or iodine have high tendency to stabilize by coordination with the free p-electron pair of a second (identical or different) heteroatom.[20–25] Such interactions are represented by a 2σ–1σ* three-electron bond and are formed inter- as well as intra-molecularly.[14] The stability of such species depends not only on the structure of the substrate but also on the difference in the electronegativity, which causes destabilization due to an asymmetric electron density distribution between the two interacting heteroatoms.[22]

The most extensively studied species containing the 2σ–1σ* bond are those generated on one-electron transfer reaction from alkyl sulfides.[20–25] In the case of organic compounds containing iodine, 2σ–1σ* species generated on iodine–iodine and iodine–sulfur interactions have been reported.[5,6,18,22,26] The possibility of p-orbital overlap between oxidised iodine and chlorine in chloroiodoalkanes and the effect of substrate structure on its stability is reported in this paper. Depending upon the chain length between two halogen atoms (chlorine and iodine) in the molecule, the nature of p-orbital overlap between two halogen atoms and transients formed is expected to be different. Halogenated organic compounds are widely used in industry and are hazardous in nature. Studies on the nature of transients formed from alkyl halides are important for an understanding of the physicochemical processes and radiolytic mechanism. These studies are also important as free radicals from alkyl halides are implicated as the transients formed on their metabolism.[27,28]

Experimental

The solvent used was deionized 'nanopure' water (conductivity = 0.06 µΩ^{-1}). The pulse radiolysis experimental set-up employing 25 and 50 ns pulses of 7 MeV electrons from a linear accelerator has been fully described elsewhere.[29] Aerated aqueous solutions of KSCN (10 mmol dm^{-3}) were used to monitor the dose delivered per pulse using $G\varepsilon_{500}$ = 21 522 dm^3 mol^{-1} cm^{-1} for 100 eV for the transient $(SCN)_2^{\cdot-}$.[30] The AC conductivity changes produced on pulse radiolysis were monitored in a dual functional cell arrangement and electronic detection system obtained from the Hahn Meitner Institute, Berlin.[31] The dose per pulse was ~1.0 × 10^{17} eV cm^{-3}. The reaction of ·OH radicals at pH > 3.5 was studied in N_2O-saturated solutions where e_{aq}^- are quantitatively converted to ·OH radicals (N_2O + e_{aq}^- ⟶ N_2 + ·OH + OH^-) with $G(OH)$ = 5.6 (species per 100 eV). At pH < 3.5, the reaction was studied in O_2-saturated solutions [$G(OH)$ = 2.9] where H and e_{aq}^- would be scavenged by O_2. The pulse radiolysis experiments are carried out at room temperature (23 °C). The error limit for rate constant measurements is within ± 10%.

1-Chloro-3-iodopropane (99%) and chloroiodomethane (97%) were obtained from Aldrich Chemicals. These were washed several times with aqueous sodium sulfite and then with distilled water to remove any trace of free iodine. The solutions of these chloroiodoalkanes were always freshly prepared just before the experiment. Independent analysis of an aqueous solution of these chloroiodoalkanes showed the absence of free iodine[32,33] and pulse radiolysis experiments supported these results. All other chemicals used were of the highest purity and were used as such.

Results

Reaction of ·OH *Radicals with* 1-*Chloro-3-iodopropane at* pH > 5.—Fig. 1(a) shows the transient optical absorption spectrum obtained immediately after pulse radiolysis of an N_2O-saturated aqueous solution of 1-chloro-3-iodopropane, CIP, (1.0 × 10^{-3} mol dm^{-3}, pH = 6.0, dose = 9.9 × 10^{16} eV cm^{-3} per pulse). It shows absorption bands with λ_{max} = 315 and 345 nm. The entire spectrum decayed by first-order kinetics with $t_{\frac{1}{2}}$ = 1.5 µs, suggesting it to be due to one species only. The absorption spectrum was not observed in the presence of 1.0 mol dm^{-3} *tert*-butyl alcohol, an ·OH radical scavenger, suggesting it to be due to reaction of ·OH radicals with the
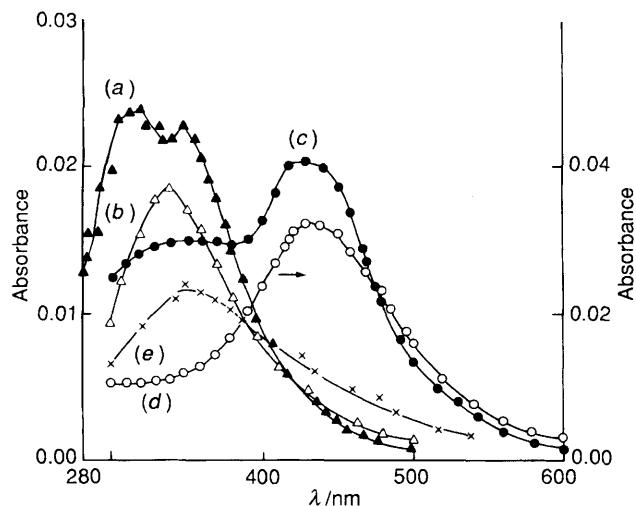
Fig. 1 Transient optical absorption spectrum recorded immediately after a 50 ns pulse in an N_2O-saturated aqueous solution of CIP; (a) 1.0×10^{-3} mol dm^{-3}, pH = 6.0, dose = 9.9×10^{16} eV cm^{-3} per pulse; (b) 1.2×10^{-4} mol dm^{-3}, pH = 3.5, dose = 8.1×10^{16} eV cm^{-3} per pulse; (c) 6.0×10^{-3} mol dm^{-3}, pH = 3.5, dose = 8.1×10^{16} eV cm^{-3} per pulse; (d) O_2-saturated solution of CIP (6.0×10^{-3} mol dm^{-3}) in $HClO_4$ (6.4 mol dm^{-3}, dose = 1.0×10^{17} eV cm^{-3}) and (e) O_2-saturated solution of CIP (1.4×10^{-4} mol dm^{-3}) in $HClO_4$ (6.4 mol dm^{-3}). The right hand axis refers to (d) only.
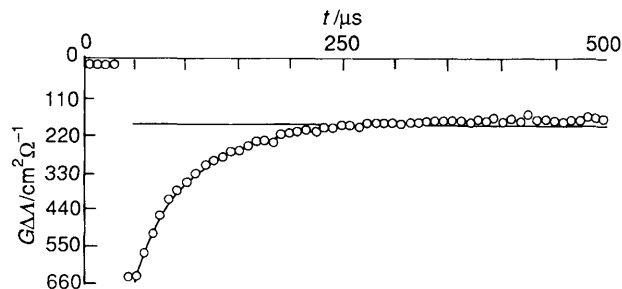
Fig. 2 Conductivity–time signal obtained on pulse radiolysis of an N_2O-saturated aqueous solution of CIP (pH = 3.5, 1.2×10^{-4} mol dm^{-3}, dose = 8.1×10^{16} eV cm^{-3} per pulse)
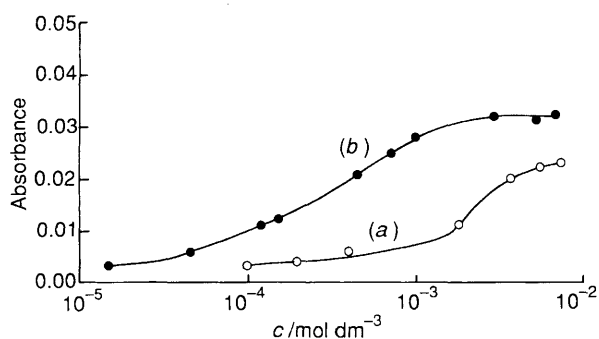
Fig. 3 Variation in the absorbance of the 430 nm band as a function of solute concentration, on pulse radiolysis of (a) an N_2O-saturated solution of CIP (pH = 3.5) and (b) an O_2-saturated solution of CIP in 6.4 mol dm^{-3} $HClO_4$. Dose = 1.0×10^{17} eV cm^{-3} per pulse.

substrate. The rate constant for the reaction of $^{\bullet}OH$ radicals with CIP is measured by monitoring the growth at 350 nm as a function of solute concentration. From the linear dependence of the rate of formation of this transient with solute concentration, the bimolecular rate constant is determined to be 4.7×10^{9} dm^{3} mol^{-1} s^{-1}. Under these experimental conditions, *the* reactivity of $^{\bullet}OH$ radicals (rate constant × concentration) towards CIP and $^{\bullet}OH$ radicals is 4.7×10^{6} and 4.6×10^{4} s^{-1}, respectively, showing that almost all the $^{\bullet}OH$ radicals have reacted with CIP to form the transient species [Fig. 1(a)].

Therefore, the concentration of $^{\bullet}OH$ radicals (9.2×10^{-6} mol dm^{-3}) could be taken equal to the concentration of the transient species. The extinction coefficient is thus determined to be 2.46×10^{3} dm^{3} mol^{-1} cm^{-1} at 350 nm.

The intensity of the transient band remained independent of solute concentration (5.0×10^{-4}–4.0×10^{-3} mol dm^{-3}) and reduced to $\sim\frac{1}{2}$ in O_2-saturated solutions without affecting the decay. The transient species could not be due to a carbon-centred radical, which is expected to react readily with oxygen. The conductivity of the solution does not change upon irradiation; therefore, the transient species must be of neutral character. Considering the electrophilic nature of $^{\bullet}OH$ radicals and published results on $^{\bullet}OH$ radical reactions with alkyl iodides, the transient species is attributed to an OH-adduct.[2,5] The $^{\bullet}OH$ radical-induced reaction with CIP could not be carried out at pH > 6.0 owing to hydrolysis of the solute, and pulse radiolysis studies gave a characteristic absorption band of I_2^{-} with $\lambda_{max} = 385$ nm. The absence of a transient band at 385 nm and the good first-order decay of the transient bands [Fig. 1(a)] at pH = 6.0 support the suggestion that the bands are not due to reaction of $^{\bullet}OH$ radicals with I^{-}, which might have been produced as a result of hydrolysis of CIP in aqueous solution. Therefore, the hydrolysis of CIP at pH = 6.0, within the experimental time (20 min), may produce $I^{-} < 1.0 \times 10^{-5}$ mol dm^{-3}. Higher concentration of I^{-} would show high reactivity with $^{\bullet}OH$ radicals to form I_2^{-}.

Reaction of $^{\bullet}OH$ Radicals with 1-Chloro-3-iodopropane at pH < 5.—The nature of the transients produced on reaction of $^{\bullet}OH$ radicals with CIP (pH < 5) depends both on the concentration of solute and pH of the solution. Fig. 1(b) shows the transient optical absorption spectrum obtained immediately after pulse radiolysis of an N_2O-saturated aqueous solution of CIP (1.2×10^{-4} mol dm^{-3}, pH = 3.5, dose = 8.1×10^{16} eV cm^{-3} per pulse). It exhibits an absorption band with $\lambda_{max} = 340$ nm. The bimolecular rate constant for the reaction of $^{\bullet}OH$ radicals with CIP forming a 340 nm band, determined by formation kinetic studies, was 2.2×10^{10} dm^{3} mol^{-1} s^{-1}. Time-resolved conductivity studies show that the formation of optically-absorbing species is accompanied by loss in conductance (Fig. 2). The formation of solute radical cation is associated with OH^{-}, which in acidic solutions would neutralise with H^{+} and result in decrease of conductance of the solution as highly conducting H^{+} ions are replaced by a normal cationic species.

The net decrease in the equivalent conductance due to the formation of cationic species would be equal to $_{-}\Lambda_{H^{+}} + \Lambda_{CIP^{+}}$. The equivalent conductance of H^{+} ions is equal to 315 cm^{2} Ω^{-1} and that of CIP^{+} is assumed to be equal to 50 cm^{2} Ω^{-1} (average value for a normal monovalent cation).[34] The net decrease in the equivalent conductance would be equal to -265 cm^{2} Ω^{-1}. From the observed value of $G\Delta\Lambda = -660$ cm^{2} Ω^{-1}, $G(CIP^{+})$ is determined to be 2.5. This is much lower than $G(OH) = 5.6$ in N_2O-saturated solutions. The remaining fraction of $^{\bullet}OH$ radicals may be forming a neutral OH-adduct. The decay of the 340 nm band was not of good first-order, which also indicates the presence of two species.

As the solute concentration is increased, the absorbance at 340 nm decreases and another transient band is observed to grow at 430 nm. Fig. 1(c) shows the transient optical absorption spectrum obtained immediately after pulse radiolysis of an N_2O-saturated aqueous solution of CIP (pH = 3.5, 6.0×10^{-3} mol dm^{-3} dose = 8.1×10^{16} eV cm^{-3} per pulse). Fig. 3(a) shows the variation in intensity of the 430 nm band as a function of CIP concentration. The absorbance reaches a plateau value for 6.0×10^{-3} mol dm^{-3} concentration of CIP. The time-resolved conductivity signal was similar to that shown in Fig. 2. This shows that a positively-charged species is formed at high
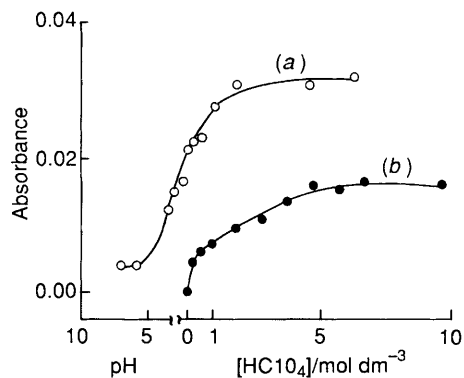
Fig. 4 Variation in the absorbance of the 430 nm band formed on pulse radiolysis of an O_2-saturated solution of CIP (6.0×10^{-3} mol dm^{-3}, dose $= 1.0 \times 10^{17}$ eV cm^{-3} per pulse) as (a) a function of H^+ ion concentration; (b) chloroiodomethane (4.5×10^{-3} mol dm^{-3}, $\lambda = 440$ nm)
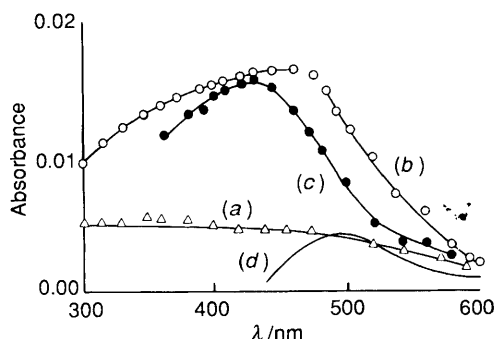
Fig. 5 Transient optical absorption spectrum recorded immediately after pulse radiolysis of an O_2-saturated solution of CIM (a) pH = 2.0, 4.5×10^{-3} mol dm^{-3}; (b) $HClO_4 = 6.0$ mol dm^{-3}, 4.5×10^{-3}; (c) $HClO_4 = 6.0$ mol dm^{-3}, 4.5×10^{-4} mol dm^{-3} and (d) difference of spectra of (b) and (c). Dose $= 7.7 \times 10^{16}$ eV cm^{-3} per pulse.
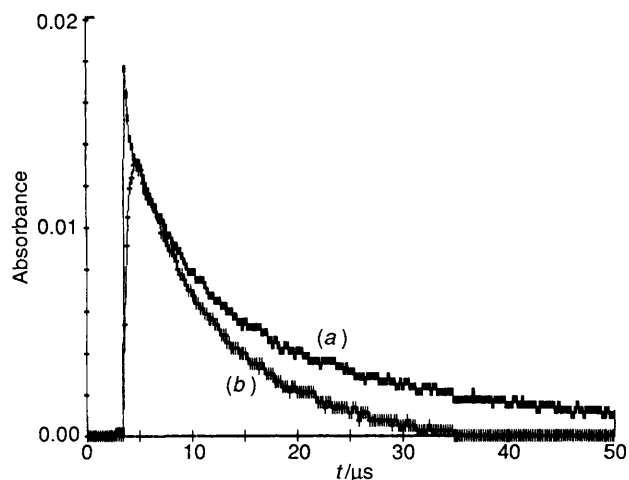
Fig. 6 Absorption–time curves obtained on pulse radiolysis of an O_2-saturated aqueous solution of CIM in 6.0 mol dm^{-3} $HClO_4$ (a) CIM $= 4.5 \times 10^{-3}$, $\lambda = 460$ nm; (b) 2.5×10^{-4} mol dm^{-3}, $\lambda = 400$ nm

solute concentration and its yield is equivalent to that at low solute concentration. Since its intensity (430 nm) increases with solute concentration, it must be due to dimer radical cations. The concentration of the transient species absorbing at 430 nm could be taken as being equal to $G(CIP^+) = 2.5$. This gives the extinction coefficient value of 5.5×10^3 dm^3 mol^{-1} cm^{-1} at 430 nm. The value is close to that reported for dimer radical cations of n-alkyl iodides.[5] A lower yield of dimer radical cations and broad absorption in the 320–380 nm region shows that at pH $= 3.5$, all the $\cdot OH$ radicals are not able to react by an electron-transfer reaction mechanism.

Due to inherent limitations of the conductivity technique at pH < 3.0,[31] the variation in the yield of dimer radical cation as a function of pH could not be studied by a pulsed conductivity method. However, the yield of dimer radical cations could be studied by monitoring the absorbance of the 430 nm band as a function of pH. Such studies could not, however, be carried out in N_2O-saturated solutions since at pH < 3.0, e^-_{aq} would also react with H^+ ions in addition to its reaction with N_2O, and $G(OH)$ would not remain constant. This difficulty could be overcome if pulse radiolysis studies were carried out in O_2-saturated solutions, in which O_2 scavenged e^-_{aq} and H^+.

Fig. 4(a) shows the variation in the absorbance of the 430 nm band of the dimer radical cation of CIP, formed on pulse radiolysis of an O_2-saturated aqueous solution of CIP (6.0×10^{-3} mol dm^{-3}, dose $= 1.0 \times 10^{17}$ eV cm^{-3} per pulse) as a function of H^+ ion concentration. The absorbance increases reaching a plateau value for a 5.5 mol dm^{-3} concentration of $HClO_4$. Fig. 3(b) shows the variation in the absorbance of the 430 nm band formed on pulse radiolysis of an O_2-saturated aqueous solution ($HClO_4 = 6.4$ mol dm^{-3}, dose $= 1.0 \times 10^{17}$ eV cm^{-3} per pulse) of CIP as a function of solute concentration. The plateau value is observed for 6.0×10^{-3} mol dm^{-3} concentration of CIP. Fig. 1(d) shows the optical absorption spectrum obtained immediately after pulse radiolysis of an O_2-saturated aqueous solution of CIP (6.0×10^{-3} mol dm^{-3}) in 6.4 mol dm^{-3} $HClO_4$. This exhibits only one band with $\lambda_{max} = 430$ nm. Under these conditions, the band is observed to decay by first-order kinetics with $t_\frac{1}{2} = 16.0$ μs. Considering $G(OH) = 2.9$, the extinction coefficient of this transient band (430 nm) is determined to be 6.7×10^3 dm^3 mol^{-1} cm^{-1}. This value is slightly higher than that determined by conductivity studies.

As the concentration of CIP is lowered, the absorbance at 430 nm decreases whereas such a decrease is not observed in the region of 340 nm. Fig. 1(e) shows the transient optical absorption spectrum obtained immediately after pulse radiolysis of an O_2-saturated aqueous solution of CIP (1.4×10^{-4} mol dm^{-3}) in 6.4 mol dm^{-3} $HClO_4$. The band with $\lambda_{max} = 345$ nm is observed to decay by first-order kinetics with $t_\frac{1}{2} = 4.0$ μs. The extinction coefficient is determined to be 2.41×10^3 dm^3 mol^{-1} cm^{-1}. This band must be due to a simple iodine centre radical cation of CIP.

Reaction of $\cdot OH$ Radicals with Chloroiodomethane.—Fig. 5(a) shows the transient optical absorption spectrum obtained on pulse radiolysis of an O_2-saturated aqueous solution of chloroiodomethane, CIM, (pH $= 2.0$, 4.5×10^{-3} mol dm^{-3}). The absence of any transient band (300–600 nm) shows that $\cdot OH$ radicals are not able to react with CIM to form either OH-adducts or radical cations. The OH-adduct and radical cations of n-alkyl iodides are known to absorb in this region.[5] As the H^+ ion concentration is increased, absorption in the region of 400–500 nm begins. Fig. 4(b) shows the variation in the absorbance (440 nm) of the transient band formed on pulse radiolysis of an O_2-saturated aqueous solution of CIM (4.5×10^{-3} mol dm^{-3}) as a function of H^+ ion concentration. Absorbance increases with H^+ ion concentration, reaching a plateau value after 6.0 mol dm^{-3} $HClO_4$. Fig. 5(b) shows the transient spectrum obtained immediately after pulse radiolysis of an O_2-saturated aqueous solution of CIM (4.5×10^{-3} mol dm^{-3}, dose $= 7.7 \times 10^{16}$ eV cm^{-3} per pulse) in 6.0 mol dm^{-3} $HClO_4$. Broad absorption is observed in the region of 300–480 nm. A typical absorption–time signal (460 nm) is shown in Fig. 6(a). It exhibits initial sharp decay followed by relatively slower decay. From the observed spectrum [Fig. 5(b)] and decay curve [Fig. 6(a)], it appears that the spectrum consists of two species. The absorbance at 430 nm remained nearly independent of solute concentration (2.5×10^{-4}–6.5×10^{-4} mol dm^{-3}) whereas at 500 nm, it increased with solute concentration (6.5×10^{-4} —

4.5×10^{-3} mol dm^{-3}). Fig. 5(c) shows the transient optical absorption spectrum obtained immediately after pulse radiolysis of an O_2-saturated aqueous solution of CIM (4.5×10^{-4} mol dm^{-3}) in 6.0 mol dm^{-3} HClO$_4$. It decayed by first-order kinetics with $t_{\frac{1}{2}} = 8.0$ μs [Fig. 6(b)]. Good first-order decay suggests it to be due to one species only. The extinction coefficient is determined to be 2.63×10^3 dm^3 mol^{-1} cm^{-1}. The bimolecular rate constant for the reaction of ·OH radicals forming the 430 nm band is determined to be 4.0×10^9 dm^3 mol^{-1} s^{-1}. Fig. 5(d) shows the difference in the absorption spectrum of 5(b) and 5(c), which shows a band with $\lambda_{max} = 500$ nm.

Discussion

The transient optical absorption spectrum [Fig. 1(a)] obtained on reaction of ·OH radicals with CIP must be due to the OH-adduct formed with the I atom of CIP, eqn. (1), since 1-chloro-

$$I-(CH_2)_3-Cl + \cdot OH \longrightarrow Cl-(CH_2)_3 I \cdot . \cdot OH \quad (1)$$
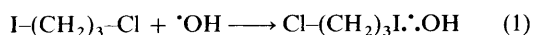
propane failed to form a similar spectrum on reaction with ·OH radicals. Moreover, the OH-adduct formed on reactions of ·OH radicals with n-alkyl iodides has a similar absorption spectrum and is assigned to a three-electron bonded species of the type RI∴OH.[5]

Effect of pH.—At pH < 5.0, ·OH radicals react with CIP by an electron-transfer reaction mechanism. At pH = 3.5, the yield of cationic species is 2.5, much lower than $G(OH) = 5.6$ in N$_2$O-saturated solutions, although the reactivity of ·OH radicals towards CIP is sufficiently higher (4.7×10^6 s^{-1}) than with ·OH radicals (4.6×10^4 s^{-1}). The yield of cationic species (2.5) at pH = 3.5 is still lower than that observed for n-alkyl iodides (3.5).[5] This shows that chlorine is able to reduce the electron density at iodine in CIP and lowers the probability of oxidation of CIP by ·OH radicals.

At pH = 3.5, the decrease in conductivity is explained as being due to the formation of solute radical cations, since a similar decrease in conductivity with organic iodides in aqueous solutions has been attributed to their radical cations.[5,6] Since pulse radiolysis of an N$_2$O-saturated aqueous solution (pH = 3.5) of chloropropane failed to produce transient absorption similar to that shown in Fig. 1(d) and a decrease in conductivity, the ·OH radical-induced reaction with CIP must be with an iodine atom. Therefore, the decrease in conductivity in acidic solutions (pH = 3.5) is attributed to acid-catalysed oxidation of CIP according to reaction (2).

$$Cl-(CH_2)_3-I + \cdot OH + H^+ \longrightarrow Cl-(CH_2)_3-I^{\cdot+} + H_2O \quad (2)$$

The acid-catalysed oxidation of CIP by ·OH radicals could be either by reaction of H$^+$ with an OH-adduct or direct reaction of ·OH radicals with CIP (in the presence of H$^+$). In the former case, the growth of radical cation would follow the decay of OH-adduct. Such studies could not be carried out as both the transients absorb in the same region. However, a high rate constant value for the reaction of ·OH radicals with CIP (pH = 3.5) suggests that it might be produced by direct reaction of ·OH radicals. A similar conclusion was also drawn from the ·OH radical-induced reaction with iodoalkanes.[18] At pH = 3.5, ∼45% of ·OH radicals react with CIP and form an iodine-centred simple radical cation and the remaining ∼55% react to form the OH-adduct. The decay of the 340 nm band was not of good first-order decay, which suggests that the OH-adduct, which also absorbs in this region, is present along with the simple iodine-centred radical cation. At pH = 3.5, although the plateau value for the 430 nm band is observed at 6.0×10^{-3} mol

dm^{-3}, appreciable absorption is observed at 340–390 nm. This could be due to the OH-adduct. This shows that at pH = 3.5, the acid-catalysed oxidation of CIP by ·OH radicals is not complete. But when the H$^+$ ion concentration is increased, complete oxidation is possible. At low solute concentrations, simple iodine-centred radical cations are formed, which are converted to the dimer radical cation of CIP at high solute concentration. The broad absorption band of the OH-adduct, observed at 340 nm at pH = 3.5, is not seen at high H$^+$ ion concentrations [Fig. 1(d)]. The band at 340 nm [Fig. 1(e)] is assigned to simple iodine-centred radical cations since its λ_{max} is close to the λ_{max} of radical cations of n-alkyl iodides.[5] Therefore, it could not be due to the intramolecular radical cation (A) formed on p-orbital overlap of oxidized iodine and chlorine.

Effect of Solute Concentration.—The oxidized iodine has a high tendency to stabilize by coordination with another atom having a free p-electron pair. In the present case, intramolecular p-orbital overlap between oxidized iodine and chlorine does not seem to take place as the intensity of the 430 nm band was dependent on solute concentration. The intramolecular p-orbital overlap between iodine and chlorine would form a five-membered ring configuration (A), which is expected to be

A
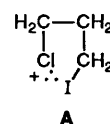
reasonably stable. The intensity would remain independent of solute concentration. The large difference in the electronegativity of iodine (2.66) and chlorine (3.16)[35] may lower the probability of p-orbital overlap between iodine and chlorine. The increase in the intensity of the 430 nm band with solute concentration may also suggest that radical cations are converted to dimer radical cations according to the equilibrium (3).

$$Cl-(CH_2)_3-I + Cl-(CH_2)_3-I^{\cdot+} \rightleftharpoons [Cl-(CH_2)_3-I]_2^{\cdot+} \quad (3)$$
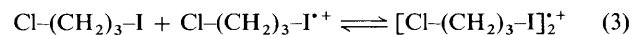
The position of the dimer radical cation, $(CIP)_2^{\cdot+}$, is close to the reported value of λ_{max} for dimer radical cations of n-alkyl iodides. In the case of CIM, the intensity at 500 nm was observed to increase with solute concentration ($6.5 \times 10^{-4} - 4.5 \times 10^{-3}$ mol dm^{-3}); it is therefore assigned to intermolecular dimer radical cations, equilibrium (4).

$$ClCH_2I + ClCH_2I^{\cdot+} \rightleftharpoons (ClCH_2I)_2^{\cdot+} \quad (4)$$
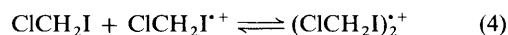
Initial sharp decay of the transient band [Fig. 6(a)] at high solute concentration (4.5×10^{-3} mol dm^{-3}) may also suggest that radical cations are reacting with solute molecules. Due to the close proximity of both the bands ($\lambda_{max} = 430$ and 500 nm) and low solubility of CIM, time-resolved studies could not be carried out so as to obtain the distinct band of dimer radical cations of CIM.

Effect of a Chlorine Atom.—The slightly lower yield of radical cation (2.5) observed for CIP in comparison with the value of 3.5 observed for n-alkyl iodides may be due to the presence of chlorine in the molecule. Although it is separated by three carbon atoms from iodine, it is expected to lower the electron density at iodine to a very small extent. This explains the slightly lower value (2.5) for $G(CIP^+)$ as compared to $G(RI^+) = 3.5$.[5] In CIM, chlorine is present at the same carbon and is expected to decrease the electron density on iodine to a considerable extent. This may be the reason for not observing the OH-adduct and radical cation, even at pH = 2.0. At high H$^+$ ion concentration, ·OH radicals are able to undergo one-electron

transfer and form solute radical cations. In this case too, oxidation is only expected at iodine. In the presence of a chlorine atom, oxidized iodine can stabilize either by coordination with a chlorine atom intramolecularly or with another iodine atom by intermolecular association. In the first case, the intensity is expected to remain independent of solute concentration and in the second case, the intensity would increase with concentration. The broad absorption [Fig. 5(b)] suggests that both types of p-orbital overlap are taking place. Since the intensity of the 430 nm band [Fig. 5(c)] was nearly independent of solute concentration ($2.5 \times 10^{-4} - 6.5 \times 10^{-4}$ mol dm^{-3}), it is assigned to the intramolecular radical cation formed by p-orbital overlap of oxidized iodine with chlorine, species **B**. It

B
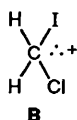
may not be due to a simple iodine-centred radical cation since they absorb at 330 nm.[5]

If we consider that the absorption band of the iodine-centred radical cation is due to an n $\longrightarrow$ σ^* transition, the presence of an electronegative chlorine atom in CIM may decrease the energy level and thus a red shift would be expected. There is, however, no direct evidence at present to prove that the chlorine atom may not show such a large red shift in the absorption maxima (340–430 nm) if the band is due to a simple iodine-centred radical cation. At most, there may be a slight red shift in the absorption maxima. On the other hand, the position of the transient band (430 nm) which is assigned to the intramolecular radical cation of CIM is close to the intramolecular radical cation formed from 1,n-diiodoalkanes.[6] Therefore, the possibility of formation of the intramolecular radical cation of CIM may not be ruled out. There may also be some contribution from the simple iodine-centred radical cation of CIM.

The 'OH radical-induced oxidation of organic compounds such as 1,3,5-trimethoxybenzene,[36] tetramethylethylene[37] and iodo compounds[5,6,18,19] have also been observed in acidic solutions but at different pK values. This shows that H$_3$O$^+$ present in acidic solutions may not be the oxidizing species responsible for the oxidation of CIP and CIM. In such a case, oxidation should have occurred at the same H$^+$ ion concentration. HO$_2$ radicals present in O$_2$-saturated acidic solutions are also oxidizing species, but these radicals cannot be oxidizing CIP and CIM since the oxidation potential for HO$_2$ radicals is $+1.0$ V,[38] whereas even Br$_2^{\cdot-}$, whose redox potential is $+1.6$ V, is unable to oxidize CIP and CIM. The transient absorption was not observed in the presence of 'OH radical scavenger (tert-butyl alcohol), even though HO$_2$ radicals would be present at high concentrations. Therefore, the observed oxidation of CIP and CIM in acidic solutions is as according to reaction (2). The difference in the observed H$^+$ ion concentration required for the oxidation may be due to the difference in electron density at iodine.

Conclusions

In 1-chloro-3-iodopropane, the chlorine is able to reduce slightly the electron density at iodine and thus lowers the probability of its oxidation by 'OH radicals in acidic solution. The oxidized iodine is unable to form an intramolecular radical cation by p-orbital overlap with the free p-electrons of chlorine and instead forms intermolecular dimer radical cations. In chloroiodomethane, 'OH radicals are unable to undergo one-electron transfer reactions when the H$^+$ ion concentration is <0.2 mol dm^{-3}. At higher H$^+$ ion concentrations, oxidation is

possible and the oxidized iodine is able to self-stabilize by intramolecular coordination with the free p-electron of chlorine at low solute concentrations to form intramolecular radical cations. At high solute concentrations the oxidized iodine stabilizes by coordination with the free p-electron pair of another iodine atom intermolecularly and so form dimer radical cations.

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