Formation of Radical Cations of Polyiodomethanes: A Pulse Radiolysis Study

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The transient optical absorption band (λ_{max} = 380 nm, $t_{\frac{1}{2}}$ = 23 μs and ε = 2 010 dm^3 mol^{-1} cm^{-1}) produced on pulse radiolysis of N_2O-saturated aqueous solution of CH_2I_2 (pH 6.0) has been assigned to the OH adduct radical, $CH_2I_2{\cdot}OH$. In acidic aqueous solutions, $CH_2I_2^+$ (λ_{max} = 380 and 570 nm, $t_{\frac{1}{2}}$ = 3 μs and ε_{570} = 2 150 dm^3 mol^{-1} cm^{-1}) has been identified as the intermediate. The rate constants for the reaction of OH radicals with CH_2I_2 to form $CH_2I_2{\cdot}OH$ and $CH_2I_2^+$ have been determined to be 2.1×10^9 and 6.0×10^9 dm^3 mol^{-1} s^{-1} respectively. Cl_2^- has been found to oxidize CH_2I_2 to $CH_2I_2^+$ with a bimolecular rate constant of 1.7×10^8 dm^3 mol^{-1} s^{-1}. $CH_2I_2^+$ is a good oxidant and oxidizes I^-, Br^-, and methyl disulphide with high rate constants close to the diffusion limit. I_2 is the main stable end product formed on γ-radiolysis and its yield is equal to $\frac{1}{2}$ G($-CH_2I_2$). The transient optical absorption bands observed on pulse radiolysis of CH_2I_2 and CHI_3 in 1,2-dichloroethane have been assigned to $CH_2I_2^+$ (λ_{max} = 380 and 590 nm) and CHI_3^+ (λ_{max} = 400 and 610 nm).

In the past the nature of transient intermediates formed on γ-radiolysis and photolysis of alkyl halides in hydrocarbon glasses at low temperatures has been assessed from the effect of known hole and electron scavengers.[1–5] The radical cations of these compounds have been inferred to be formed on charge transfer from solvent cation to the solute. Independent experimental evidence for the formation of radical cations have also come from time-resolved studies using pulse radiolysis and laser flash photolysis,[6–8] e.s.r.,[9] and mass spectrometric investigations.[10,11] The OH radicals are strongly oxidizing species but they have been inferred to react with alkyl iodides in aqueous solutions forming an OH adduct.[12,13] Recently, employing the pulse-radiolysis technique with optical and conductivity detection, radical cations have been identified as the transient intermediates formed on reaction of OH radicals with organic iodides in aqueous solutions.[14–16] The OH radical-induced reactions with CH_2I_2 are reported in this paper. In order to overcome uncertainties arising from low solubility and possible hydrolysis of polyiodomethanes in aqueous solutions, complimentary studies have also been carried out in 1,2-dichloroethane.

Studies on the spectral characteristics and oxidizing behaviour of radical cations of alkyl iodides are helpful in understanding the mechanism of radiolytic decomposition of these compounds. The unpaired p electron of the oxidized iodine atom has a high tendency to interact with the free p-electron pair of the second heteroatom (either I or another atom). Such interactions (intermolecular or intramolecular) have been shown to exist between two iodine atoms in alkyl iodides and 1,*n*-di-iodoalkanes respectively.[14,15] But the p-orbital overlap between two iodine atoms located on the same carbon atom has not been reported so far. The results of studies on the formation of radical cations of CH_2I_2 and CHI_3 and the possibility of p-orbital overlap between two iodine atoms in these polyiodomethanes are reported in this paper.

Experimental

The solvents used were deionized Nanopure water (conductivity = 0.06 μΩ^{-1}) and 1,2-dichloroethane (Koch-Light, purity >99%). All other chemicals were of the purest grade (purity >99%) and were used as such. The pulse-radiolysis experimental set-up employing 25 ns pulses of 7 MeV electrons from a linear accelerator has been fully described elsewhere.[17] The conductivity changes in the solution produced as the result of pulse radiolysis were monitored in the dual function cell arrangement and electronic detection system obtained from Hahn Meitner Institute, Berlin.[18,19] The observed signal (ΔV) is related to the equivalent molar conductance change (Λ) by equation (1)[19] where V is the applied voltage between the

$$\Delta V = \frac{VR_a}{K_c\,10^3}\sum_n c_n z_n \Lambda_n \qquad (1)$$

two electrodes (10 V), R_a the working load resistance (1 kΩ), K_c the cell constant (0.145 cm^{-1}), c_n the concentration of the *n*th charged species (mol dm^{-3}) formed after the pulse and z_n the net change in its charge (1 for one-electron oxidation). The dosimetry in this cell was carried out by monitoring of the voltage signal (ΔV) and optical absorbance at 500 nm produced on pulse radiolysis of N_2O-saturated aqueous solution of KSCN (pH 3.0). The equivalent conductance of H^+ and SCN^- ions at 25 °C are 349 and 66 Ω^{-1} cm^2 respectively.[20] The net change in the equivalent conductance of the solution due to pulse radiolysis would be −415 Ω^{-1} cm^2. The observed conductivity signal of 65 mV and absorbance of 0.025 ($G\varepsilon$ = 43 200 dm^3 mol^{-1} cm^{-1} per 100 eV) gave a value of 2.3×10^{16} eV cm^{-3} for the absorbed dose. Steady state γ-radiolysis experiments were carried out in a ^{60}Co γ-source the dose rate of which was 1.5×10^{17} eV cm^{-3} min^{-1}. The aqueous solutions (pH ⩾3.0) were generally saturated with N_2O to convert e^-_{aq} into OH radicals by the reaction [equation (2)].

$$N_2O + e^-_{aq} \longrightarrow N_2 + OH + OH^- \qquad (2)$$

I_2 formed as stable end product was estimated as I_3^- by extracting the hexane layer (obtained on extracting the aqueous solution with hexane) with aqueous KI and determining the absorbance of I_3^- at 352 nm. H_2O_2 was estimated in the aqueous extract by Ghormley's method.[21] Methyl iodide and CH_2I_2 were estimated by gas chromatography using 2 m × 0.5 cm stainless steel column filled with 10% SE 30 on chromosorb W and electron capture detector.

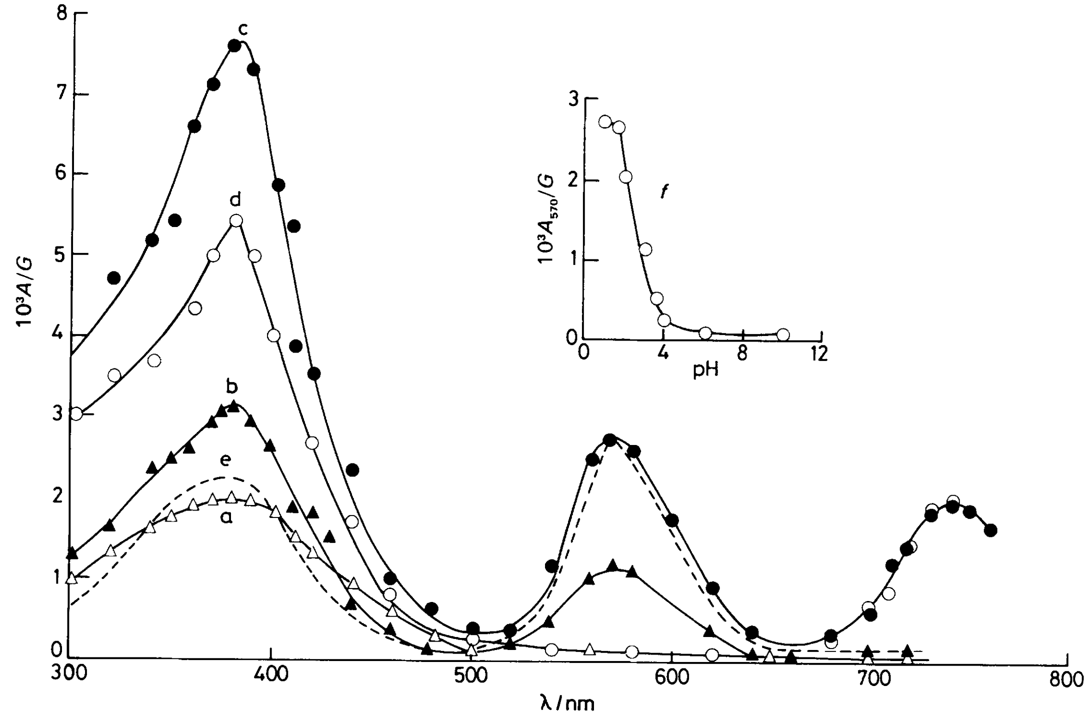

Figure 1. Transient optical absorption spectrum immediately after pulse radiolysis of CH_2I_2 (0.4 mmol dm^{-3}) in (*a*) N_2O-saturated aqueous solution (pH 6.0); (*b*) N_2O-saturated aqueous solution (pH 3.0); (*c*) O_2-saturated aqueous solution (pH 1.5); (*d*) O_2-saturated aqueous solution of I^- (3.0×10^{-5} mol dm^{-3}, pH 1.5); (*e*) difference of absorption spectrum of (*c*) and (*d*); and (*f*) variation in the absorbance at 570 nm in O_2-saturated solution of CH_2I_2 (0.4 mmol dm^{-3}) with pH.

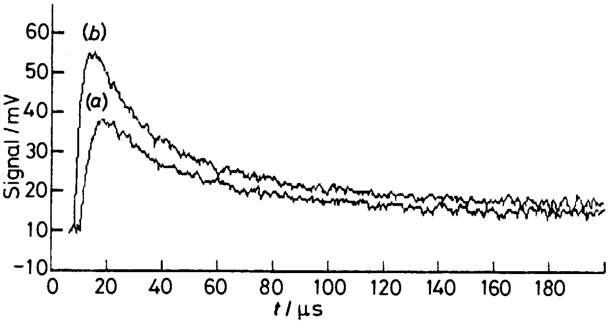

Figure 2. Absorption–time curves obtained on pulse radiolysis of N_2O-saturated aqueous solutions of CH_2I_2 (0.4 mmol dm^{-3}) (*a*) pH 6.0 and (*b*) pH 3.0.

Results and Discussion

Figure 1(*a*) shows the transient optical absorption spectrum obtained immediately after pulse radiolysis of N_2O-saturated aqueous solution of CH_2I_2 (0.4 mmol dm^{-3}, pH 6.0). The transient band (λ_{max} = 380 nm) was found to decay by first-order kinetics with $t_{\frac{1}{2}}$ = 23 μs [Figure 2(*a*)]. This band was not observed in presence of large excess of OH radical scavenger (tertiary butyl alcohol), indicating it to be due to the reaction of OH radicals with CH_2I_2. In O_2-saturated aqueous solution, except for the decrease in absorbance values by a factor of *ca.* 2, the nature of the transient spectrum was similar to the one in N_2O-saturated solution shown in Figure 1(*a*). The bimolecular rate constant for the reaction of OH radical with CH_2I_2 was determined from the absorbance build-up at 380 nm to be 2.1×10^9 dm^3 mol^{-1} s^{-1}. The overall rate constant for the reaction of OH radical with CH_2I_2 was also determined by pulse radiolysis competition kinetic method using KSCN [$K_{SCN^-+OH} = 1.1 \times 10^{10}$ dm^3 mol^{-1} s^{-1}] as standard solute.[22] The value so obtained is 1.4×10^9 dm^3 mol^{-1} s^{-1}. The somewhat lower value obtained by the pulse-radiolysis competition kinetic method using CNS^- as standard solute may reflect the possibility of oxidation of CNS^- to $CNS_2^{-\bullet}$ (the absorbance of which is measured at 500 nm) by the species formed from reaction of OH with CH_2I_2.

Under the experimental conditions employed the reactivities (*kc*) of OH towards OH radicals and CH_2I_2 are 3.9×10^4 and 4.0×10^5 s^{-1} respectively, indicating that 90% of OH radicals are available for reaction with CH_2I_2. The concentration of OH radicals produced per pulse in N_2O-saturated aqueous solutions at the dose employed is 9.8×10^{-6} mol dm^{-3}. The absorbance at 380 nm was 0.0177, which gave an extinction coefficient of 2 010 dm^3 mol^{-1} cm^{-1} on the assumption that all (90%) the OH radicals react with CH_2I_2.

On pulse radiolysis of N_2O-saturated solution (pH 6.0) there was no difference in the radiation-induced conductivity change with and without CH_2I_2 present. Hence the above transient band is assigned to a neutral species. Since its rate of formation is diffusion controlled, it would probably preclude any abstraction and substitution processes which are usually associated with some activation energy. The transient band is, therefore, assigned to the OH adduct, CH_2I_2•OH. Such a species is expected to be formed by p-orbital overlap of the unpaired p electron of OH radical with the free p electrons of iodine in CH_2I_2 forming a neutral three-electron bonded species $ICH_2I \therefore OH$. Neutral three-electron bonded species of this type have been identified in the case of reaction of OH radical with alkyl iodides[14] and of halogen atoms with organic sulphides.[23,24]

The nature of the transient absorption spectrum, decay kinetics and conductivity changes remained independent of pH over the region 6.0–10.0. However at pH 3.0, the conductivity after pulse radiolysis of N_2O-saturated aqueous solution of CH_2I_2 [Figure 3(*b*)] decreased as compared with the conductivity changes observed in the case of N_2O-saturated water at the same pH [Figure 3(*a*)]. In analogy with similar

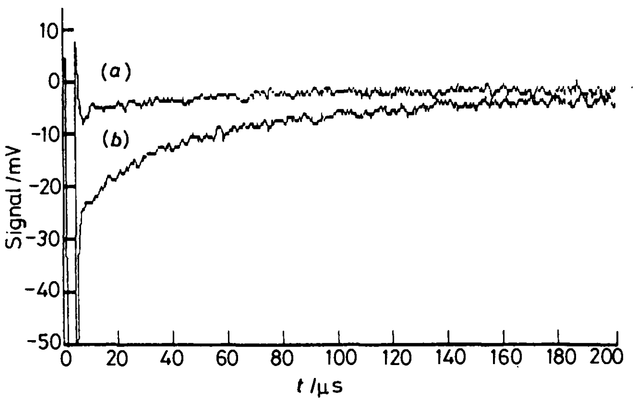

Figure 3. Conductivity–time curves obtained on pulse radiolysis of N_2O-saturated (*a*) water (pH 3.0) and (*b*) aqueous solution of CH_2I_2 (0.4 mmol dm^{-3}, pH 3.0).

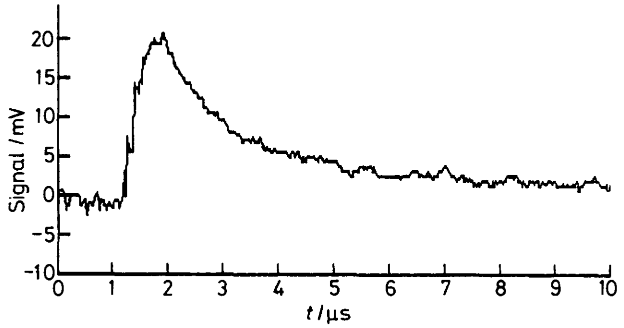

Figure 4. Absorption–time curve on pulse radiolysis of N_2O-saturated aqueous solutions of CH_2I_2 (0.6 mmol dm^{-3}, pH 3.0, 570 nm).

studies on organic iodides in aqueous solutions,[14–16] the decrease in the conductivity is explained as being due to the formation of $CH_2I_2^+$ according to equation (3).

$$CH_2I_2 + OH + H^+ \longrightarrow CH_2I_2^+ + H_2O \quad (3)$$

The net decrease in the equivalent conductance due to the formation of $CH_2I_2^+$ would be equal to $-\Lambda H^+ + \Lambda CH_2I_2^+$. The equivalent conductance of H^+ ions at 25 °C is equal to 349 cm^2 Ω^{-1},[20] and that of $CH_2I_2^+$ is assumed to be about the same as that of $C_{17}H_{38}N^+$ (21 cm^2 Ω^{-1}) because both the ions have almost the same molecular weight (268 and 256 respectively) and, therefore, may have the same mobility. Therefore, the net change in the equivalent conductance due to the formation of $CH_2I_2^+$ would be -328 cm^2 Ω^{-1}. The observed decrease in the conductivity of 18 mV (Figure 3) correponds to 7.9×10^{-7} mol dm^{-3} of $CH_2I_2^+$, from which $G(CH_2I_2^+)$ is calculated to be 2.1.

The transient species formed on pulse radiolysis of N_2O-saturated aqueous solution (pH 3.0) of CH_2I_2 exhibits an absorption band with $\lambda_{max} = 570$ nm [Figure 1(*b*)]. The absorbance at 570 nm was independent of CH_2I_2 concentration in the range of 2.0×10^{-4}–6.0×10^{-4} mol dm^{-3}. Higher solute concentrations could not be employed due to solubility limitations. The radical cations of alkyl iodides absorb at 320 nm and dimer radical cations, which are formed at much higher solute concentrations (1.0×10^{-3}–1.0×10^{-2} mol dm^{-3}), absorb at $\lambda > 420$ nm.[14] The transient absorption band at 570 nm observed for low concentrations of CH_2I_2 may be due to solute radical cations, $CH_2I_2^+$, with some contribution from dimer radical cations. This band was observed to decay by first-order kinetics with $t_{\frac{1}{2}} = 3$ µs (Figure 4). The bimolecular rate constant for the reaction of OH radicals with CH_2I_2 forming the 570 nm band was determined from its formation kinetics to be 6.0×10^9 dm^3 mol^{-1} s^{-1}. The overall rate constant for the reaction of OH radicals with CH_2I_2 at pH 3.0 was also determined from pulse radiolysis competition kinetics using KSCN as the standard solute, which gave value of 4.1×10^9 dm^3 mol^{-1} s^{-1}. In this case also the somewhat lower value may be due to the oxidation of CNS^- by $CH_2I_2^+$. At this pH, the rate constant value determined by competition kinetics may have some contribution from the reaction of OH radicals with CH_2I_2 forming OH adduct as all the OH radicals are not able to oxidise CH_2I_2 to $CH_2I_2^+$. However, the rate constant value determined from the build up at 570 nm would be free from such interference as the OH adduct has no absorption at 570 nm.

From the experimentally measured transient absorbance at 570 nm and taking $G(CH_2I_2^+) = 2.1$, the extinction coefficient was estimated to be 2 150 dm^3 mol^{-1} cm^{-1}. The lower yield of $CH_2I_2^+$ suggests that not all the OH radicals are able to react with CH_2I_2 forming $CH_2I_2^+$ at pH 3.0. The presence of 380 nm band [Figure 1(*b*)] can be taken to infer that remaining OH radicals have reacted to form $CH_2I_2{\cdot}OH$. But the decay of 380 nm band [Figure 2(*b*)] was not similar to that of the $CH_2I_2{\cdot}OH$ at 380 nm [Figure 2(*a*)] or $CH_2I_2^+$ at 570 nm (Figure 4). It is possible that $CH_2I_2^+$ may also have an absorption band in the region of 380 nm. In O_2-saturated solutions, the nature of the transient optical absorption spectrum was similar to that of N_2O-saturated solution. The overall absorption was lowered due to lower OH yield in O_2-saturated solution.

Due to inherent limitation of the conductivity technique at pH <3.0,[19] the variation in the yield of $CH_2I_2^+$ with pH could not be studied by the conductivity method. However, such studies could be carried out by optical absorption measurements at 570 nm as a function of pH. Since at lower pH, e^-_{aq} also reacts with H^+ ions in addition to its reaction with N_2O, G(OH) would not remain constant in N_2O-saturated solutions at pH <3.0. This difficulty was overcome by studying the variation in the absorbance at 570 nm with pH in O_2-saturated solution at different pH. Figure 1(*f*) shows transient absorbance changes at 570 nm on pulse radiolysis of O_2-saturated aqueous solution of CH_2I_2 as a function of pH of the solution. The inflexion point is observed at pH 2.7. The formation and decay kinetics of the 570 nm band at pH 1.5 were similar to those observed at pH 3.0 in N_2O-saturated solutions. Therefore, the species formed in the acidic solutions is also assigned to $CH_2I_2^+$. From the measured absorbance and the extinction coefficient of 2 150 dm^3 mol^{-1} cm^{-1} for $CH_2I_2^+$, the $G(CH_2I_2^+)$ was determined to be 2.46. Under these conditions this is close to G(OH) = 2.9 in O_2-saturated aqueous solution at pH 1.5. The bimolecular rate constant for the reaction of OH radicals with CH_2I_2 at pH 1.5 was determined by pulse-radiolysis competition kinetics using KSCN as standard solute, which gave the value of 5.8×10^9 dm^3 mol^{-1} s^{-1}. The rate constant value determined from the build up of 570 nm band was 6.3×10^9 dm^3 mol^{-1} s^{-1}.

Figure 1(*c*) shows the transient optical absorption spectrum on pulse radiolysis of O_2-saturated aqueous solution of CH_2I_2 (pH 1.5). The transient band at 740 nm was observed to decay with kinetics similar to that observed on pulse radiolysis of O_2-saturated aqueous solution of I^- (2×10^{-5} mol dm^{-3}, pH 1.5). Therefore, the band at 740 nm must be due to I_2^-.[25] I_2^- has another absorption band at 380 nm. But the 380 nm band [Figure 1(*c*)] did not decay by pure second-order kinetics similar to that of I_2^-, therefore, it may not be entirely due to I_2^-. It is possible that an absorption band of $CH_2I_2^+$ is also present in this region. The $CH_2I_2^+$ absorption at 380 nm is also observed on pulse radiolysis of N_2O-saturated aqueous solution of CH_2I_2 at pH 3.0. I_2^- may be formed by the reaction of OH radical with I^-, which may be produced as a hydrolysis

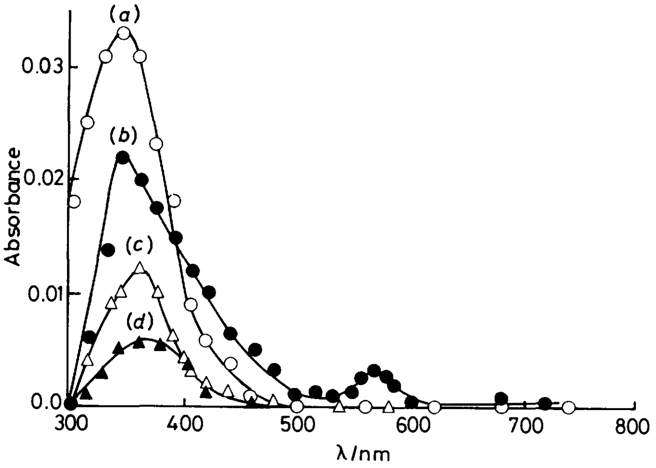

Figure 5. Transient optical absorption spectrum on pulse radiolysis of N_2O-saturated aqueous solutions of (*a*) Cl^- (40 mmol dm^{-3}, pH 3.0), (*b*) in presence of CH_2I_2 (0.4 mmol dm^{-3}) immediately after the pulse, (*c*) 20, and (*d*) 40 μs after the pulse.

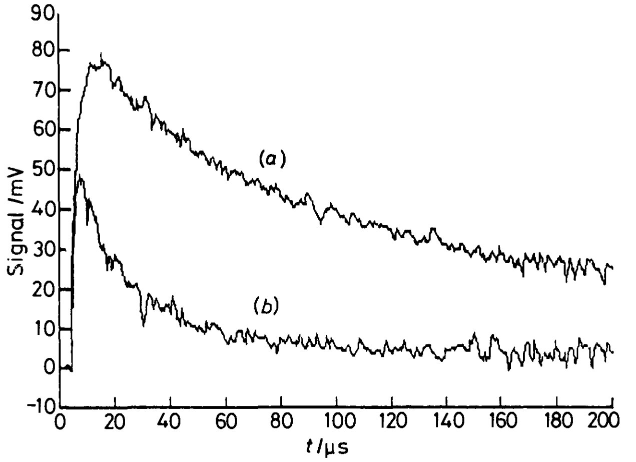

Figure 6. Decay of 345 nm band of Cl_2^- (*a*) in the absence of CH_2I_2 (*b*) in the presence of CH_2I_2 (0.4 mmol dm^{-3}).

product. Experiments showed that I^- is produced by the hydrolysis of CH_2I_2 at pH 1.5 and the concentration of I^- was estimated to be 2×10^{-5} mol dm^{-3} within half an hour of storage of a 0.4 mmol dm^{-3} solution of CH_2I_2. Within this time, hydrolysis was negligible at pH > 3.0.

Figure 1(*d*) shows the transient optical absorption spectrum obtained on pulse radiolysis of an O_2-saturated aqueous solution of I^- (3.0×10^{-5} mol dm^{-3}, pH 1.5). The transient bands at 380 and 740 nm are assigned to I_2^-.[25] Since the absorbance at the 740 nm band formed on pulse radiolysis of an O_2-saturated aqueous solution of I^- [Figure 1(*d*)] and CH_2I_2 [Figure 1(*c*)] is almost the same, the contribution of I_2^- at 380 nm in the absorption spectrum shown in Figure 1(*c*) must be equal to the absorption of I_2^- at 380 nm shown in Figure 1(*d*). The difference in the absorption spectrum shown in Figure 1(*c*) and 1(*d*) would be due to $CH_2I_2^+$ [Figure 1(*e*)]. This shows absorption bands at 380 and 570 nm. An attempt was made to obtain the true spectrum of $CH_2I_2^+$ at pH 1.5 by reducing the hydrolysis of CH_2I_2 by decreasing the pre-irradiation time to 10 min. This was achieved by preparing the solution of CH_2I_2 at pH 6.0 and then adjusting the pH of the solution to 1.5 just before irradiation. Even by this technique, the hydrolysis of CH_2I_2 to give I^- prior to irradiation could not be completely avoided.

The growth of $CH_2I_2^+$ (570 nm) does not follow the decay of CH_2I_2·OH (380 nm) suggesting that $CH_2I_2^+$ is not formed by the reaction of H^+ with CH_2I_2·OH. The growth of the 570 nm band formed on pulse radiolysis of O_2-saturated aqueous solution of CH_2I_2 was observed to be independent of the pH of the solution, except that its absorption decreased with increase in pH [Figure 1(*f*)], suggesting that OH radicals react directly with CH_2I_2 (in the presence of H^+) to form $CH_2I_2^+$. Formation of $CH_2I_2^+$ has, therefore, been explained as acid-catalysed oxidation of CH_2I_2. Alternatively, we may consider H_3O^+ as the reactive oxidizing species in acidic solutions. The OH radical induced oxidation of organic compounds such as 1,3,5-trimethoxybenzene,[26] tetramethylethylene,[27] iodobenzene,[16] and methyl iodide[14] has also been observed in acidic aqueous solutions. If H_3O^+ were the oxidizing species then 'p*K*' for the formation of radical cations of different organic compounds would have been almost the same. But the observed 'p*K*' for the formation of radical cations of the above organic compounds are 4.2, 2.2, 2.7, and 3.5 respectively. Therefore, H_3O^+ could not be considered as the general oxidizing species responsible for the formation of radical cations of organic compounds in acidic aqueous solutions.

Another way of generating solute radical cations in aqueous solutions is by the use of specific one-electron oxidants. It was possible to observe oxidation of CH_2I_2 by Cl_2^- whereas Br_2^- and Tl^{2+} were not able to oxidize this compound. Figure 5(*a*) shows the transient optical absorption spectrum obtained on pulse radiolysis of N_2O-saturated aqueous solution of Cl^- (40 mmol dm^{-3}, pH 3.0). The transient band (λ_{max} = 345 nm) was observed to decay by second-order kinetics [Figure 6(*a*)]. In the presence of CH_2I_2 (0.4 mmol dm^{-3}) the decay was faster and first-order [Figure 6(*b*)]. The decay was studied at different concentrations of CH_2I_2 (1.0×10^{-4}–5.0×10^{-4} mol dm^{-3}) and from the slope of the linear plot of the pseudo-first-order rate constant *versus* the CH_2I_2 concentration the bimolecular rate constant was evaluated to be 1.7×10^8 dm^3 mol^{-1} s^{-1}. The transient optical absorption spectrum [Figure 5(*b*)] showed a band at 570 nm, which must be due to $CH_2I_2^+$ formed on oxidation of CH_2I_2 by Cl_2^-. The absorption spectrum on complete decay of Cl_2^- showed another broad band in the region of 360–380 nm [Figure 5(*c*), (*d*)]. It must also be due to $CH_2I_2^+$. The distinct band of $CH_2I_2^+$ could not be seen immediately after the pulse [Figure 5(*b*)], due to its overlap with that of Cl_2^-.

The fact that CH_2I_2 could be oxidized by OH radicals at low pH and by Cl_2^- but not by Tl^{2+} or Br_2^-, suggests that the reduction potential of the couple $CH_2I_2^+/CH_2I_2$ would be in the range of 2.0–2.3 V *vs.* NHE. Hence $CH_2I_2^+$ could be considered as a strong oxidant. The oxidation of I^- by $CH_2I_2^+$ was studied by monitoring of the decay of the 570 nm band of $CH_2I_2^+$ in presence of various concentrations of I^- (3.0×10^{-6}–6.0×10^{-5} mol dm^{-3}). From the slope of the linear plot of the pseudo-first-order decay constant *versus* I^- concentration the bimolecular rate constant was calculated to be 6.4×10^9 dm^3 mol^{-1} s^{-1}. The formation of the product band of I_2^- at 380 nm could not be inferred due to the presence of $CH_2I_2^+/CH_2I_2$·OH bands at the same wavelength. However, the growth of the product transient band of I_2^- at 740 nm was observed. But due to low absorption at 740 nm, the rate constant for the oxidation of I^- by $CH_2I_2^+$ could not be estimated accurately from the build up of 740 nm band.

Another class of compound which are easily oxidized are the organic disulphides. The oxidation of methyl disulphide by $CH_2I_2^+$ was studied both by following the decay of the 570 nm band of $CH_2I_2^+$ and the formation of $CH_3SS^+CH_3$ band at 460 nm.[28] The 570 nm band decayed faster in the presence of methyl disulphide (4.5×10^{-5}–9.5×10^{-5} mol dm^{-3}). The bimolecular rate constant as evaluated from the slope of linear

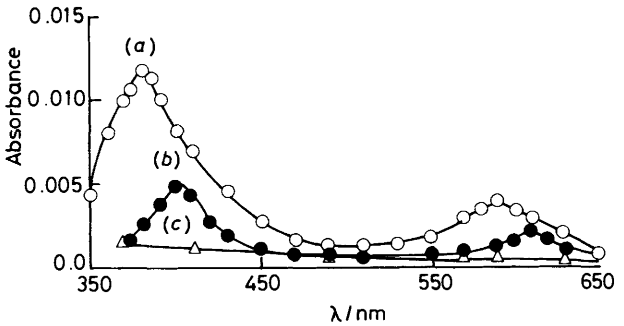

Figure 7. Transient optical absorption spectrum obtained on pulse radiolysis of N_2 saturated (*a*) CH_2I_2 (4.2 mmol dm^{-3}) in DCE; (*b*) CHI_3 (2.3 mmol dm^{-3}); (*c*) DCE.

plot of the pseudo-first-order decay constant as a function of concentration of the sulphur compound is 8.1×10^9 dm^3 mol^{-1} s^{-1}. Simultaneously, another absorption band at 460 nm was observed to grow from which the bimolecular rate constant was estimated to be 1.0×10^{10} dm^3 mol^{-1} s^{-1} and this is close to the value determined from the decay of $CH_2I_2^+$ band. The 570 nm band of $CH_2I_2^+$ was also observed to decay faster in the presence of Br^- (3.5×10^{-5} mol dm^{-3}), indicating its oxidation. The bimolecular rate constant estimated from the decay of 570 nm band was 7.7×10^9 dm^{-3} mol^{-1} s^{-1}. Tl^{2+} failed to oxidize CH_2I_2 to $CH_2I_2^+$. The radical cation of CH_3I was also observed to act as a strong oxidizing agent.[29] Experiments were carried out to determine whether $CH_2I_2^+$ could oxidize Tl^+ to Tl^{2+} by monitoring of the decay of 570 nm band in presence of increasing concentrations of Tl^+ (2.2×10^{-6}–4.4×10^{-5} mol dm^{-3}). The decay was not affected by addition of Tl^+ indicating that $CH_2I_2^+$ is not able to oxidize Tl^+. These studies suggest that the reduction potential of the $CH_2I_2^+/CH_2I_2$ couple may be in the region of 2.0 V *vs.* NHE.

Formation of Radical Cations in 1,2-*Dichloroethane*.—The electrons produced on γ-radiolysis of 1,2-dichloroethane (DCE)

$$CH_2Cl\text{-}CH_2Cl \longrightarrow CH_2Cl\text{–}CH_2Cl^+ + e^- \quad (4)$$

undergo a fast dissociative electron capture reaction with the matrix molecules thereby increasing the yield of matrix cations

$$CH_2Cl\text{-}CH_2Cl + e^- \longrightarrow CH_2Cl\text{–}CH_2 + Cl^- \quad (5)$$

by preventing their geminate recombination with the electrons. The ionization potential of CH_2I_2 (9.5 eV) is lower than that of DCE (11.1),[30,31] Therefore, DCE could be used for the formation of radical cations of CH_2I_2. This matrix has been recommended and used as a solvent for the study of radical cations of organic compounds.[32]

In order to ensure the unambiguous observation of $CH_2I_2^+$, pulse-radiolysis investigations were carried out in DCE. Figure 7(*a*) shows the transient optical absorption spectrum obtained on pulse radiolysis of N_2-saturated solution of CH_2I_2 in DCE. Two transient bands (λ_{max} = 380 and 590 nm) were observed, both of which decayed by first-order kinetics with $t_{\frac{1}{2}} = 5$ μs. These bands are assigned to $CH_2I_2^+$ formed on positive charge transfer from DCE^+ to CH_2I_2. These bands are not due to species formed in DCE itself since pulse radiolysis of N_2-saturated DCE alone showed very little absorption over the entire wavelength region [Figure 7(*c*)].

CHI_3 is insoluble in aqueous solutions and, therefore, its radical cation formation could not be investigated in this medium. As in the case of CH_2I_2, the radical cation of CHI_3 is expected to be formed in pulse-irradiated DCE since its ionization potential (9.3 V)[31] is also lower than that of DCE. Figure 7(*b*) shows the transient optical absorption spectrum obtained on pulse radiolysis of N_2-saturated solution of CHI_3 in DCE. Two transient bands (λ_{max} = 400, 610 nm) were observed which decayed by first-order kinetics with $t_{\frac{1}{2}} = 3$ μs. These bands are assigned to CHI_3^+ formed by charge transfer from DCE cations. Photoelectron spectroscopic data[33] on pure CH_2I_2 and CHI_3 show absorption band of their radical cations at 375 and 360 nm respectively. These bands are close to the absorption bands observed at 380 and 400 nm in DCE. Therefore, the assignment of the observed bands in our investigations as due to $CH_2I_2^+$ and CHI_3^+ respectively is reasonable. The band at 375 nm observed on matrix photoionization studies of CH_2I_2 in argon at 15 K is also assigned to $CH_2I_2^+$.[3] Photoelectron spectroscopic data do not show absorption bands in the region of 590 and 610 nm observed by us for $CH_2I_2^+$ and CHI_3^+ in DCE matrix. These bands could not be assigned to dimer radical cation as they were observed at low solute concentration and aggregation of polar solutes in polar solvent at room temperature is also not expected to take place.

Intramolecular p electron orbital overlap between unpaired p electron of oxidized iodine atom with free p electron pair of second iodine atom has been observed for 1,*n*-di-iodoalkanes (with $n \geqslant 2$).[15] For n = 3–6, the optical transition is observed at 405, 435, 445, and 455 nm respectively. The iodine–iodine distances in these compounds are calculated to be 6.0, 7.4, 8.3, and 10.2 Å respectively.[34] These are higher than the iodine–iodine molecule bond length of 2.6 Å. At such a large separation, the p-orbital overlap between two iodine atoms may not be possible. But due to the possibility of formation of a more stable ring configuration on bending of carbon–carbon chains, p-orbital overlap between two iodine atoms may be possible. The possibility of formation of such a ring structure would decrease as the number of CH_2 groups between two iodine atoms increases. This is reflected in the decreasing yield, life times and transition energy of the intramolecular radical cation observed for 1,*n*-di-iodoalkanes (n = 3–6).[15] In 1,2-di-iodoethane, the iodine–iodine distance is 4.9 Å (less than 6.0 Å for 1,3-di-iodopropane), but the optical transition is observed at 550 nm. In this case, much larger bending of carbon–carbon chains is required to form a four-membered ring structure, which may be less likely to take place. Therefore, p-orbital overlap between two iodine atoms in 1,2-di-iodoethane may be very small resulting in the red-shifted transient absorption band observed for the radical cation of this compound. In di-iodomethane, the iodine–iodine distance is 3.6 Å, lower than for all other 1,*n*-di-iodoalkanes. But the optical transition for the radical cation was observed at 570 nm, higher than in the case of the other di-iodoalkanes. In this case p-orbital overlap would be very small, thus explaining the further red-shift in the transient optical absorption bands for $CH_2I_2^+$ and CHI_3^+ as compared with the radical cations of other di-iodoalkanes.

γ-*Radiolytic Studies*.—On γ-radiolysis of N_2O-saturated aqueous solution of CH_2I_2 (0.4 mmol dm^{-3}, pH 6.0), the stable end products observed were CH_3I and I_2. The possible mechanism for the formation of stable products is shown in equations (6)–(8). The observed yield of $G(\text{–}CH_2I_2)$ is 5.3, which

$$CH_2I_2 + OH \longrightarrow CH_2I_2{\cdot}OH \quad (6)$$

$$CH_2I_2{\cdot}OH \longrightarrow {\cdot}CH_2I + \tfrac{1}{2}I_2 + \tfrac{1}{2}H_2 + \tfrac{1}{2}O_2 \quad (7)$$

$$CH_2I + CH_2I \longrightarrow CH_3I + CHI \quad (8)$$

is close to G(OH) in N_2O-saturated water at pH 6.0. The observed value of $G(I_2)$ is 2.45, close to the expected value of

$\frac{1}{2}G(-CH_2I_2) = 2.65$. $G(H_2O_2)$ is 0.7 close to the value for pure water. These results are in accord with the proposed reaction mechanism. The observed yield of CH_3I is 0.16. If CH_2I radicals decay only by process (8), then $G(CH_3I)$ would be equal to $\frac{1}{4}G(I_2) = 0.6$. But the observed yield of CH_3I was lower indicating that CH_2I may also decay by some other process which at present could not be assigned due to lack of knowledge of all of the stable end products. $CH_2I_2^+$, formed on radiolysis of O_2-saturated aqueous solution of CH_2I_2 (0.4 mmol dm^{-3}, pH 1.5), is shown to dissociate by reaction (9).[3]

$$CH_2I_2^+ \longrightarrow CH_2I^+ + \tfrac{1}{2}I_2 \qquad (9)$$

The observed value of $G(-CH_2I_2)$ is 2.3. This is close to $G(CH_2I_2^+) = 2.5$ evaluated by pulse radiolysis in the present work. The observed value of $G(I_2)$ is 1.31, which is close to the expected value of $\frac{1}{2}G(CH_2I_2^+) = 1.25$ on the basis of reaction (9). The yield of CH_3I was 0.36. The exact mechanism for the decay of CH_2I^+ to give CH_3I and any other unidentified radiolysis product is not yet known.

Conclusions

The OH radicals are shown to react with CH_2I_2 to form $CH_2I_2{\cdot}OH$ in basic and neutral aqueous solutions and $CH_2I_2^+$ in acidic solutions. The oxidation of CH_2I_2 could also be achieved by Cl_2^- but not by Br_2^- or Tl^{2+}. $CH_2I_2^+$ is a strong oxidant (E^0 *ca.* 2.0 V *vs.* NHE) and has been shown to oxidize Br^-, I^-, and methyl disulphide with high rate constant values.

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