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J. CHEM. SOC. FARADAY TRANS., 1993, 89(3), 477-483

Pulse Radiolysis Study on Radical Cations of Alkyl Bromides in Aqueous Solutions

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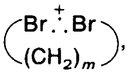
The transient optical absorption bands formed on reaction of $^{\bullet}OH$ radicals with 1,*m*-dibromoalkanes and *n*-alkyl bromides in acidic aqueous solutions have been assigned to intra-,



$\left(\overset{+}{Br\therefore Br}\right)(CH_2)_m$, and inter-molecular, $(RBr\therefore BrR)^+$, radical cations, respectively. Depending upon R, these radical cations exhibit an optical absorption band in the 385–450 nm region. Increases in the chain length and electron-releasing power of R results in a red shift of λ_{max} and a decrease in the lifetime. These radical cations are strong oxidants and oxidize various substrates with bimolecular rate constants of the order of 10^9 dm^3 mol^{-1} s^{-1}.

Halogenated hydrocarbons are frequently employed as drugs, solvents, pesticides and for the study of electron-transfer reactions in radiation and electrochemical investigations.[1–7] Many of these compounds are hazardous, toxic and cause environmental problems. Therefore, it is important to know the identity and the reactivity of the transient species produced from these halogenated hydrocarbons in different environmental conditions. These studies are also useful since halogenated hydrocarbons are considered to play an important role in depletion of tropospheric ozone.[8] A large number of radiation and photochemical investigations have been carried out on the nature and reactivity of transients produced from chloroalkanes.[1–5] In the case of bromoalkanes, very little information is available on the nature and reactivity of transients produced in different environmental conditions. Pulse radiolysis studies of neat bromoalkanes and their solutions in hydrocarbons have revealed the formation of bromine atoms, which form complexes with parent compounds, and the reactivity of these complexes have been determined with a number of organic compounds.[6] The transient species formed on photolysis and radiolysis of bromo compounds in a glassy matrix at 77 K have been studied by following the effects of known hole and electron scavengers and assigned to solute radical cations formed on charge transfer from solvent to solute.[9–12] Experimental evidence for the formation of solute radical cations of bromoalkanes have also come from EPR,[13] mass spectrometry[14] and picosecond pulse radiolysis techniques.[15] Pulse radiolysis studies on bromo compounds in aqueous solutions have mainly been carried out with e_{aq}^-, by which dissociative electron capture results in the formation of Br^-.[16,17] The $^{\bullet}OH$ radicals are shown to react with bromoalkanes by H-atom abstraction and form a radical species absorbing at a wavelength < 280 nm.[18,19] The transient optical absorption band formed on reaction of $^{\bullet}OH$ radicals in neutral aqueous solution of *t*-butyl bromide has recently been assigned to an OH-adduct, although it contained appreciable contribution from $Br_2^{\bullet -}$.[20] The $^{\bullet}OH$ radicals are strong oxidizing species, but they fail to undergo one-electron transfer reactions with bromoalkanes in aqueous solutions.[21] Even strong one-electron oxidants such as $Cl_2^{\bullet -}$ are unable to form solute radical cations of bromoalkanes in aqueous solutions.[22] Recently, we have reported the conditions under which $^{\bullet}OH$ radicals can undergo one-electron transfer reactions with bromoalkanes in aqueous solutions.[23] We have carried out pulse radiolysis of ethyl bromide and 1,3-dibromopropane in acidic aqueous solutions ($HClO_4 \geqslant 4.0$ mol dm^{-3}) and the transient optical absorption bands observed at 410 and 385 nm, respectively, were assigned to their solute radical cations.[23] The present paper is based on the results of pulse radiolysis studies of acidic aqueous solutions of several bromoalkanes by optical absorption measurements.

The radical cations of aliphatic compounds containing a hetero function such as sulfur, nitrogen, phosphorus, oxygen, halogens have a high tendency to stabilize by coordination with the free p-electron pair of a second (identical or different) hetero atom.[24–27] Such interactions are represented by a 2σ–$1\sigma^*$ three-electron bond (two-centre, three-electron) and are formed both inter- and intra-molecularly. The most extensively studied species containing 2σ–$1\sigma^*$ are those generated on one-electron transfer reactions from alkyl sulfides.[26] In the case of bromine, the species containing 2σ–$1\sigma^*$ electrons are those generated between oxidized sulfur and bromine.[27,28] The oxidation of bromine in aqueous solutions of bromoalkanes and their possible stabilization with another bromine both inter- and intra-molecularly has not been reported so far. The formation and effect of substrate structure on the stabilization of 2σ–$1\sigma^*$ species (two-centre, three-electron bond) between two bromine atoms in aqueous solutions of bromoalkanes are discussed in this paper.

Experimental

Preparation of Solutions

The solutions were prepared in 'nanopure' deionized water. The alkyl bromides were of high purity (>98%) and were obtained from Fluka chemicals. These were purified by passing through activated alumina column. They were further washed with aqueous solution of sodium sulfite to remove any free bromine. The solutions of bromoalkanes were always freshly prepared just before each experiment. Independent analysis of an aqueous solution of these bromoalkanes showed the absence of free bromine with most of the solutes (see text). Pulse radiolysis experiments also supported these results. All other chemicals were of highest purity and used without any further purification. Perchloric acid (60%, sp.gr. = 1.53) was obtained from E. Merck. Indian oxygen 'iolar' grade N_2 or O_2 gases were used for purging the solutions. In the absence of irradiation, the stability of the bromoalkanes in acidic aqueous solutions was studied by observing the formation of Br^- as a function of time.[29] The

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results show the absence of hydrolysis of the bromoalkanes in aqueous solution within the duration of the experiment (10 min).

Irradiation

Irradiation of aqueous solutions of bromoalkanes was carried by using high-energy (7 MeV,† 50 ns) electron pulses obtained from a linear accelerator whose details have been fully described elsewhere.[30] The dose delivered per pulse was 1.0×10^{17} eV cm^{-3} as determined using a KSCN dosimeter. The reaction of $^{\bullet}OH$ radicals in acidic solutions was carried out in O_2-saturated solutions with $G(OH) = 2.9$. H atoms and e^-_{aq} are converted to $HO^{\bullet}_2$ radicals. The $HO^{\bullet}_2$ radicals are also oxidizing in nature and their contribution towards the reaction with bromoalkanes was independently studied (see text) and found to be zero. The effect of the transients produced on the direct radiolysis of $HClO_4$ was also examined in the presence of a high concentration of $HClO_4$. All experiments were carried out at room temperature (25 °C) and the error in the measurement of rate constant data is within ±10%.

Results

Reactions of $^{\bullet}$OH Radicals with 1,*m*-Dibromoalkanes

Fig. 1(*a*) shows the transient optical absorption spectrum obtained on pulse radiolysis of an O_2-saturated solution of 1,4-dibromobutane (8.3×10^{-3} mol dm^{-3}) in 5.7 mol dm^{-3} $HClO_4$. The transient band with $\lambda_{max} = 400$ nm is observed to decay by first-order kinetics with $t_{1/2} = 2.6$ μs. The intensity of this band remained independent of solute concentration in the $(1.6–8.3) \times 10^{-3}$ mol dm^{-3} range.

In acidic solutions, e^-_{aq} are converted to H atoms, which are scavenged by O_2 and produce $HO^{\bullet}_2$ radicals. This radical is also oxidizing in nature. Therefore, it is important to know the contribution of $HO^{\bullet}_2$ radicals for reaction with 1,4-dibromobutane. Pulse radiolysis studies in the presence of 0.5 mol dm^{-3} *tert*-butyl alcohol, an $^{\bullet}OH$ radical scavenger, revealed the absence of a transient absorption band in the 300–600 nm region. Under these conditions, only $HO^{\bullet}_2$ radicals would be available for reaction with 1,4-dibromobutane. In the absence of 1,*m*-dibromoalkanes, pulse radiolysis of an O_2-saturated 5.7 mol dm^{-3} $HClO_4$ solution also failed to give a transient absorption band in the 300–600 nm region. Therefore, the observed spectrum [Fig. 1(*a*)] should result from a product of the reaction of $^{\bullet}OH$ radicals with 1,4-dibromobutane.

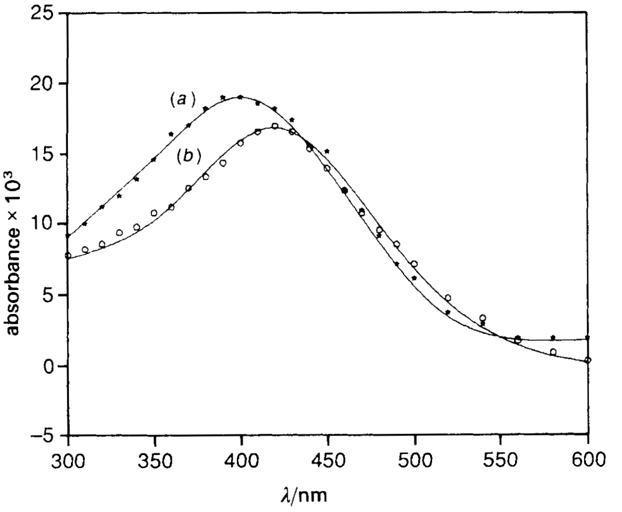

Fig. 1 Transient optical absorption spectrum obtained immediately after pulse (50 ns) radiolysis of an O_2-saturated solution of (*a*) 1,4-dibromobutane (8.3×10^{-3} mol dm^{-3}, $HClO_4 = 5.7$ mol dm^{-3}); (*b*) 1-bromopropane (1.1×10^{-2} mol dm^{-3}, $HClO_4 = 7.8$ mol dm^{-3}). Dose = 9.2×10^{16} eV cm^{-3} per pulse

The rate constant for the reaction of $^{\bullet}OH$ radicals with 1,4-dibromobutane was determined by following the formation kinetics at 400 nm for various solute concentrations. The band is observed to grow by psuedo-first-order (k_{obs}) kinetics, increasing linearly with solute concentration. The bimolecular rate constant determined from the slope of the linear plot of k_{obs} with solute concentration is 6.5×10^9 dm^3 mol^{-1} s^{-1}.

Fig. 2 shows the variation in the intensity and $t_{1/2}$ of the transient band (400 nm) formed on pulse radiolysis of an O_2-saturated solution of 1,4-dibromobutane (8.3×10^{-3}) as a function of $HClO_4$ concentration. Both the lifetime and intensity increase with $HClO_4$ concentration, reaching a plateau value at 8.0 mol dm^{-3} $HClO_4$. These curves show an inflexion point at 4.9 mol dm^{-3} $HClO_4$.

Studies on the formation of a transient band on reaction of $^{\bullet}OH$ radicals with 1,4-dibromobutane have been extended to a number of other 1,*m*-dibromoalkanes (Table 1). In each case ($m \geqslant 3$), the intensity of the transient band remained independent of solute concentration, increased with $HClO_4$ and was observed only when the concentration of $HClO_4$ was more than 3.0 mol dm^{-3}. In order to compare the lifetime and intensity of the transient band for various 1,*m*-dibromoalkanes ($m \geqslant 3$), pulse radiolysis studies were carried out at a constant dose (1.1×10^{17} eV cm^{-3}), concentration of bromide (1.5×10^{-3} mol dm^{-3}) and $HClO_4$ (7.8 mol dm^{-3}) and the results are shown in Table 1. It can be seen that the intensity and lifetime decrease with increase in the length of the chain between the two bromine atoms and the position of λ_{max} shows a red shift.

Fig. 3(*a*) shows the transient optical absorption spectrum obtained immediately after pulse radiolysis of an O_2-saturated solution of 1,2-dibromoethane (3.3×10^{-2} mol dm^{-3}) in 9.8 mol dm^{-3} $HClO_4$. Time-resolved studies showed an absorption band in the 300–400 nm region which had attained saturation value 6 μs after the pulse [Fig. 3(*b*)]. On subtracting this absorption band from Fig. 3(*a*), a broad absorption band with $\lambda_{max} = 440$ nm is observed [Fig. 3(*c*)]. The absorbance at 440 nm was found to be independent of solute concentration in the $(1.1–5.8) \times 10^{-3}$ mol dm^{-3} region whereas it increased slightly when the solute concentration was increased from 5.8×10^{-3} to 11.6×10^{-3} mol dm^{-3}. The absorbance was also observed to increase, with $HClO_4$

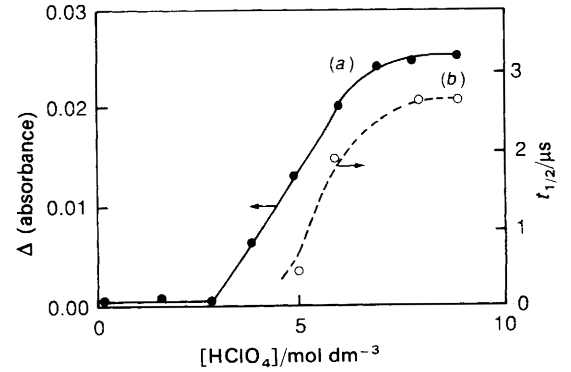

Fig. 2 Variation in (*a*) absorbance (400 nm) and (*b*) $t_{1/2}$ of the transient band formed on pulse radiolysis of an O_2-saturated solution of 1,4-dibromobutane (8.3×10^{-3} mol dm^{-3}) as a function of $HClO_4$ concentration. Dose = 1.1×10^{17} eV cm^{-3} per pulse

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† 1 eV ≈ $1.602\,18 \times 10^{-19}$ J.

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Table 1 Physical properties of the transient bands formed on pulse radiolysis of O_2-saturated solutions of 1,*m*-dibromoalkanes (1.5×10^{-3} mol dm^{-3}) in 7.8 mol dm^{-3} $HClO_4$; dose = 1.1×10^{17} eV cm^{-3} per pulse

solute	λ_{max}/nm	$\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$	$t_{1/2}/\mu s$	formation rate constant $/dm^3\ mol^{-1}\ s^{-1}$
1,3-dibromopropane	385	5460	9.9	4.1×10^9
1,4-dibromobutane	400	4770	2.6	6.5×10^9
1,5-dibromopentane	410	4460	1.9	8.5×10^9
1,6-dibromohexane	425	3250	1.4	1.7×10^{10}
1,2-dibromoethane	440	3640[a]	5.1[a]	—
dibromomethane	450	—	—	—

[a] With solute concentration at 3.3×10^{-3} mol dm^{-3}; $HClO_4$ = 9.8 mol dm^{-3}.

concentration attaining a saturation value at 9.0 mol dm^{-3} with an inflexion at 8.0 mol dm^{-3} concentration.

Pulse radiolysis of an O_2-saturated solution of dibromomethane (3.3×10^{-3} mol dm^{-3}) in 9.8 mol dm^{-3} $HClO_4$ also showed the formation of an absorption band 6 μs after the pulse, similar to that shown in Fig. 3(*b*). On subtracting this absorption from the transient absorption obtained immediately after the pulse, a broad band with λ_{max} = 450 nm was observed. The absorbance of this band was observed to remain independent of solute concentration in the low concentration region and increased with solute concentration in the higher concentration region. The absorbance also increased with $HClO_4$ concentration. A saturation value could not be observed even up to 9.8 mol dm^{-3} $HClO_4$.

Reaction of ˙OH Radicals with *n*-Alkyl Bromides

Fig. 1(*b*) shows the transient optical absorption spectrum obtained immediately after pulse radiolysis of an O_2-saturated solution of C_3H_7Br (1.1×10^{-2} mol dm^{-3}) in 7.8 mol dm^{-3} $HClO_4$. The transient band with λ_{max} = 420 nm is observed to decay by first-order kinetics with $t_{1/2}$ = 2.6 μs. The band was not observed in the presence of 0.5 mol dm^{-3} *tert*-butyl alcohol, showing that the band is due to the reaction of ˙OH radicals with C_3H_7Br and not due to the reaction of $HO_2^{\bullet}$ radicals. The intensity of this band was observed to increase with solute and $HClO_4$ concentration reaching a plateau value at 4.0×10^{-2} and 7.8 mol dm^{-3} concentration, respectively (Fig. 4). Similar transient optical absorption bands were also observed with a number of other alkyl bromides (Table 2). In each case, the variation in intensity of the transient band with solute and $HClO_4$ concentration exhibited similar behaviour, as shown in Fig. 4.

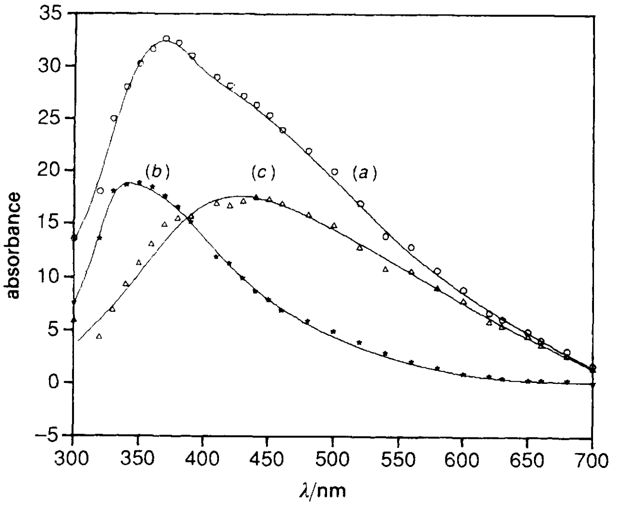

Fig. 3 Transient optical absorption spectrum obtained on pulse radiolysis of an O_2-saturated solution of 1,2-dibromoethane (3.3×10^{-3} mol dm^{-3}) in 9.8 mol dm^{-3} $HClO_4$ (*a*) immediately and (*b*) 6 μs after the pulse, (*c*) the difference of (*a*) and (*b*). Dose = 9.9×10^{16} eV cm^{-3} per pulse

On pulse radiolysis of O_2-saturated solutions of *n*-alkyl bromides [with alkyl chain lengths of four or more carbon atoms (C_x, $x \geqslant 4$) and with bromine in the side chain], an absorption band in the region of 340–380 nm was also observed. A typical optical absorption spectrum obtained immediately after pulse radiolysis of an O_2-saturated solution of isopropyl bromide (2.0×10^{-2} mol dm^{-3}) in 7.8 mol dm^{-3} $HClO_4$ is shown in Fig. 5(*a*). On subtracting the absorption [Fig. 5(*b*)] which attained saturation 6 μs after the pulse, a broad band with λ_{max} = 430 nm is observed [Fig. 5(*c*)]. The decay kinetics are studied at wavelengths where the contribution of the broad absorption is minimum. The absorbance of this band (430 nm) was found to increase with solute concentration. The absorbance was also observed to

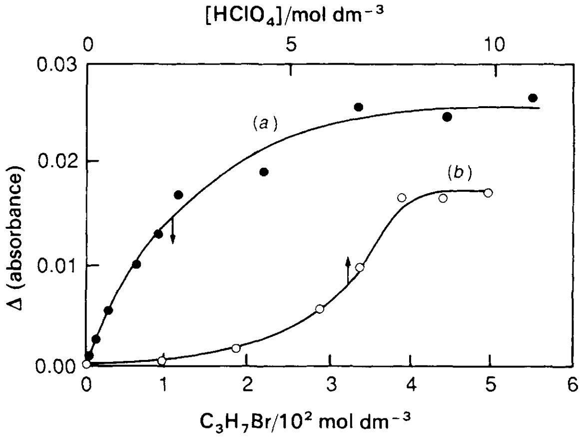

Fig. 4 Variation in the absorbance (420 nm) of the transient band formed immediately after pulse radiolysis of an O_2-saturated solution of 1-bromopropane as a function of (*a*) solute concentration ($HClO_4$ = 7.8 mol dm^{-3}) and (*b*) $HClO_4$ concentration (C_3H_7Br = 1.1×10^{-2} mol dm^{-3})

Table 2 Physical properties of the transient formed on pulse radiolysis of an O_2-saturated solution of *n*-alkyl bromides in 6.8 mol dm^{-3} $HClO_4$; dose = 1.04×10^{17} eV cm^{-3} per pulse

solute	λ_{max}/nm	$t_{1/2}/\mu s$	$\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$	σ^* [a]
bromoethane	410	2.8	6.69×10^3	−0.100
1-bromopropane	420	2.6	5.87×10^3	−0.115
1-bromobutane	435	2.3	—	−0.130
2-bromopropane	430	1.9	—	−0.200
2-bromobutane	440	1.8	—	−0.210
1-bromoheptane	450	—	—	—
bromocyclohexane	450	—	—	−0.150

[a] Ref. 47.

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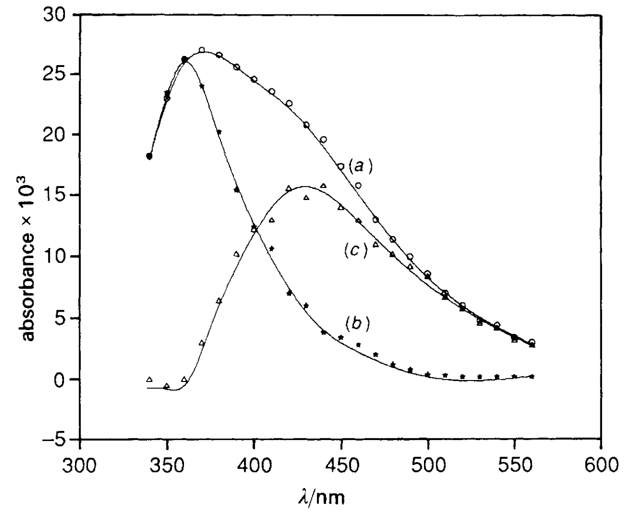
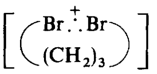


Fig. 5 Transient optical absorption spectrum obtained on pulse radiolysis of an O_2-saturated solution of 2-bromopropane (2.0×10^{-2} mol dm^{-3}) in 7.8 mol dm^{-3} $HClO_4$ (*a*) immediately and (*b*) 6 μs after the pulse, (*c*) difference of (*a*) and (*b*). Dose = 1.0×10^{17} eV cm^{-3} per pulse

increase with $HClO_4$ concentration, attaining a saturation value at 6.8 mol dm^{-3}.

The decay of the transient band formed on pulse radiolysis of an O_2-saturated solution of bromoalkanes becomes faster in the presence of small amounts of oxidizable substrate. Simultaneous with the faster decay, the growth of the absorption was also observed at the respective λ_{max} of the oxidized species as shown in Tables 3 and 4. Fig. 6 show the time-resolved absorption spectra (0 and 6 μs) after pulse radiolysis of an O_2-saturated solution of 1,3-dibromopropane (9.8×10^{-3} mol dm^{-3}) containing Cl^- (2.1×10^{-4} mol dm^{-3}) in 7.8 mol dm^{-3} $HClO_4$. The absorption band with $\lambda_{max} = 350$ nm [Fig. 6(*b*)] matches with that of $Cl_2^{\cdot -}$. Therefore, this band could be assigned to $Cl_2^{\cdot -}$ formed on oxidation of Cl^-. The transient band formed on pulse radiolysis of an O_2-saturated solution of ethyl bromide was also found to oxidize a number of substrate molecules and the bimolecular rate constants are given in Table 4. These reactions were monitored both *via* decay and formation kinetics. The rate constants are in diffusion-controlled limits.

Table 3 Rate constants for the oxidation of various substrates by



substrate	rate constant /10^{-9} dm^3 mol^{-1} s^{-1}	λ_{max}/nm	oxidized species
Br^-	6.9	360	$Br_2^{\cdot -}$
Cl^-	2.9	350	$Cl_2^{\cdot -}$
SCN^-	3.8	475	$(SCN)_2^{\cdot -}$
$(CH_3)_2S$	2.4	460	$[(CH_3)_2S]_2^{\cdot +}$
CH_3SSCH_3	1.0	430	$CH_3S^{\cdot +}SCH_3$

Table 4 Rate constants for the oxidation of various substrates by dimer radical cations of C_2H_5Br, $[C_2H_5Br\overset{+}{\therefore}BrC_2H_5]$

substrate	rate constant /10^{-9} dm^3 mol^{-1} s^{-1}	λ_{max}/nm	oxidized species
Br^-	5.6	360	$Br_2^{\cdot -}$
Cl^-	4.5	350	$Cl_2^{\cdot -}$
SCN^-	5.4	475	$(SCN)_2^{\cdot -}$
$(CH_3)_2S$	1.9	460	$[(CH_3)_2S]_2^{\cdot +}$

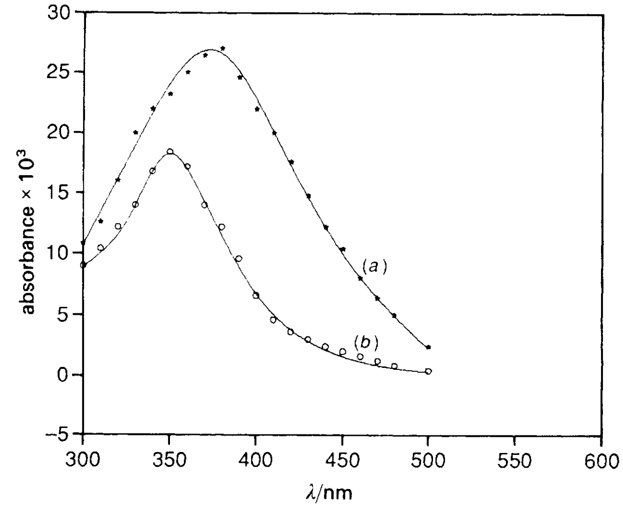


Fig. 6 Transient optical absorption spectrum obtained (*a*) 0 and (*b*) 6 μs after pulse radiolysis of 1,3-dibromopropane (9.8×10^{-3} mol dm^{-3}) and Cl^- (2.1×10^{-4} mol dm^{-3})

Discussion

Effect of $HClO_4$ Concentration

The absorption band observed at 360 nm,[20] on pulse radiolysis of N_2O-saturated neutral aqueous solution of bromoalkanes may not be due to an OH-adduct because: (1) the position of this band matches with that of $Br_2^{\cdot -}$; (2) the intensity of this band increased if pulse radiolysis is carried out with the aqueous solution, which is stored in the dark prior to pulse radiolysis; (3) time-resolved conductivity studies showed the formation of a charged species and not of a neutral OH-adduct; (4) the bimolecular rate constant for the formation of an OH-adduct is mostly in the diffusion-control limit (10^9–10^{10} dm^3 mol^{-1} s^{-1})[21] and not of the order of 10^8 dm^3 mol^{-1} s^{-1}.[20] From these studies, it appears that most probably the transient band (360 nm) reported for the OH-adduct could be due to $Br_2^{\cdot -}$.

As the H^+ ion concentration is increased, transient absorption is found to increase in the region of 400 nm. Therefore, the band could be due to the reaction of $^{\cdot}OH$ radicals with bromoalkanes, in the presence of acid. The $^{\cdot}OH$ radicals are known to undergo acid-catalysed oxidation of iodo[24,25] and a number of other organic compounds.[31–33] In the absence of acid, no transient absorption band was observed in the 350–600 nm region. Therefore, an intermediate OH-adduct is either not formed or is highly unstable. The radical cation may not be formed on acid-catalysed loss of a hydroxyl group from an OH-adduct. In the case of alkyl iodides,[24] the OH-adduct is formed, but its decay was not found to follow the growth of their radical cations formed in the presence of acid. The growth was found to be independent of H^+ ion concentration. Therefore, it is possible that acid-catalysed oxidation of bromoalkanes by $^{\cdot}OH$ radicals may be taking place, in the present case, forming solute radical cations in a single step. The reaction may be represented as follows:

$$RBr + {}^{\cdot}OH + H^+ \rightarrow RBr^{\cdot +} + H_2O \qquad (1)$$

The acid-catalysed oxidation of organic compounds is observed at different p*K* values.[24,25,31–33] This may be due to the presence of groups of different electronegativity. In the case of simple alkyl iodides, acid-catalysed oxidation is observed at pH $\leqslant$ 3.0 and at pH = 1.0, $G(RI^{\cdot +}) = G(^{\cdot}OH)$.

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Bromine has high electronegativity (2.96) compared with iodine (2.66).[34] Therefore, it is expected that acid-catalysed oxidation of bromoalkanes may require a higher acid concentration compared with that for iodoalkanes. This has actually been observed, the acid-catalysed oxidation of bromoalkanes is observed only when the acid concentration is $\geqslant 3.0$ mol dm^{-3}. It would be more difficult to oxidize chloroalkanes owing to the higher electronegativity of chlorine (3.16).[34] The $^{\bullet}$OH radical induced reactions with 1-chlorobutane failed to produce a transient band in the 300–600 nm region even in the presence of 9.8 mol dm^{-3} $HClO_4$. This supports the present conclusion that the acid-catalysed oxidation of organic compounds by $^{\bullet}$OH radicals would depend upon the electronegativity of the substituent groups.

In the case of 1,*m*-dibromoalkanes ($m \geqslant 3$), a saturation value of the absorbance of the transient band was observed when the $HClO_4$ concentration was > 3.0 mol dm^{-3}, with an inflexion point at 5.0 mol dm^{-3}. Therefore, the second bromine atom may not affect the electron density at the other bromine atom. This may be due to the longer chain length between the two bromine atoms. In 1,2-dibromoethane ($m = 2$), an inflexion point is observed at 8.0 mol dm^{-3} and a saturation value of the absorbance of the transient band is observed at 9.0 mol dm^{-3} $HClO_4$. In this case, the second bromine atom is found to lower the electron density of the other bromine atom, thus requiring higher acid concentration. In dibromomethane, the $^{\bullet}$OH radical induced acid-catalysed oxidation is not complete even when the acid concentration is 9.8 mol dm^{-3}. This shows that the lowering of the electron density at bromine by an adjacent bromine atom is more effective if the chain length between the two bromine atoms is small. On $^{\bullet}$OH radical induced oxidation of chloroiodoalkanes,[31] chlorine was observed to lower the electron density at iodine owing to the higher electron affinity of chlorine. The lowering of the electron density by chlorine was found to be influenced by the length of chain between the chlorine and iodine substituents.[31]

Pulse radiolysis of an aqueous solution containing a high concentration of $HClO_4$ may produce species such as $Cl^{\bullet}$, Cl_2, $ClO_2^{\bullet}$. Similar species may also be produced on radiolysis of an aqueous solution of $NaClO_4$. The reaction of such species with bromoalkanes was investigated *via* pulse radiolysis of an O_2-saturated solution of $NaClO_4$ (2.0 mol dm^{-3}) both in the presence and absence of 1,3-dibromopropane (1.0×10^{-3} mol dm^{-3}). The studies revealed the absence of transient bands, which were observed in the presence of $HClO_4$. These results conclusively show that the transient bands observed with different bromoalkanes (Tables 1 and 2) in the presence of $HClO_4$ are due to the reaction of $^{\bullet}$OH radicals with bromoalkanes, and not to the reaction of any other transient species with bromoalkanes.

As already mentioned, the transient band is not observed in presence of *tert*-butyl alcohol, an $^{\bullet}$OH radical scavenger, showing that $HO_2^{\bullet}$ radicals are not contributing towards the oxidation of bromoalkanes. This is expected since the oxidation potential of $HO_2^{\bullet}$ radicals is +1.0 V,[35] whereas even stronger oxidizing agents, such as $Br_2^{\bullet -}$ whose redox potential is +1.6 V, were unable to oxidize the bromoalkanes.

In neutral aqueous solutions, $^{\bullet}$OH radicals are known to react with alkyl bromides by H-atom abstraction[18] to form a radical absorbing at <280 nm, reaction (2):

$$RBr + {}^{\bullet}OH \rightarrow R(-H)Br + H_2O \qquad (2)$$

Another possible mechanism for the formation of solute radical cations is the addition of H^+ ions to the radicals formed *via* H-atom abstraction, reaction (3)

$$R(-H)Br + H^+ \rightarrow RBr^{\bullet +} \qquad (3)$$

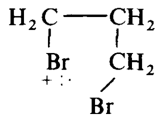
Moreover, the formation of solute radical cations by this reaction may not require such a high concentration of acid, and a high rate constant for the reaction of $^{\bullet}$OH radicals with bromoalkanes may suggest the direct reaction of $^{\bullet}$OH radicals with bromoalkanes [reaction (1)], *i.e.* not *via* radical formation [reaction (2)].

Hydrolysis of Bromoalkanes

The absorption band in Fig. 3(*b*) and Fig. 5(*b*) may be due to $Br_2^{\bullet -}$ formed by the reaction of $^{\bullet}$OH radicals with Br^-, which might have been produced during the hydrolysis of bromoalkanes. The position of this band matches with λ_{max} of $Br_2^{\bullet -}$. This absorption band was not observed in the case of *n*-alkyl bromides (C_1–C_4) and 1,*m*-dibromoalkanes ($m \geqslant 3$) showing that the hydrolysis of bromoalkanes, in general, is negligible and slower in acidic solutions. The pulse radiolysis of neutral and alkaline solutions of bromoalkanes gave a characteristic absorption band with $\lambda_{max} = 360$ nm, and independent studies showed the presence of Br^-. The absence of hydrolysis [within the duration of the experiment (10 min)] of *n*-alkyl bromides (C_1–C_4) and 1,*m*-dibromoalkanes ($m \geqslant 3$) enabled us to study the properties of the radical cations of these bromoalkanes. In other cases, as mentioned previously, hydrolysis could not be avoided. The observation of the radical cations of such bromoalkanes, where hydrolysis could not be avoided, was possible only by the use of a time-resolved spectroscopic method, which exploited the differences in the positions of λ_{max} and the lifetimes of $Br_2^{\bullet -}$ and the radical cations of the bromoalkanes.

Effect of Solute Concentration

In the case of 1,*m*-dibromoalkanes, the intensity of the transient band remained constant with solute concentration in the range $(0.1–4.0) \times 10^{-3}$ mol dm^{-3}. Therefore, the transient band could not be due to dimer radical cations. The band could not be assigned to a simple bromine-centred radical cation as pulse radiolysis of an O_2-saturated solution of C_3H_7Br (1.0×10^{-4} mol dm^{-3}) in 6.5 mol dm^{-3} $HClO_4$ did not give any transient absorption at 400 nm. It is known that the bromine atom has a strong tendency to stabilize on coordination with the free p electron pair of sulfur and form a three-electron-bonded species.[28] Oxidized iodine in 1,*m*-diiodoalkanes has also been observed to stabilize by coordination intramolecularly and form three-electron-bonded species.[25] Therefore, it is possible that oxidized bromine may also have a strong tendency to stabilize with another bromine atom and form an intramolecular radical cation (A).



A

The absorbance of such a transient species would be independent of solute concentration. The intensity of the transient band formed on pulse radiolysis of O_2-saturated solutions of 1,2-dibromoethane and dibromomethane remained independent of solute concentration in the lower concentration region and increased with solute concentration in the higher concentration region. This suggests that oxidized bromine is interacting with the second bromine atom both inter- and intra-molecularly. The relatively broad absorption band [Fig. 3(*c*)] also suggests such a possibility.

In the case of *n*-alkyl bromides, the intensity of the transient band increased with solute concentration. Therefore, it could not be assigned to a radical cation. It is possible that

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the bands could be due to dimer radical cations formed according to the following reaction:

$$\mathrm{RBr^{\bullet} + RBr \rightleftharpoons (RBr)_2^{\bullet +}} \qquad (4)$$

The increase in the intensity and lifetime of the transient band with solute concentration suggests the existence of the equilibrium. Although the formation of dimer radical cations by $^{\bullet}$OH radical induced reactions with solute dimers

$$\mathrm{(RBr)_2 + {}^{\bullet}OH + H^+ \rightarrow (RBr)_2^{\bullet +} + H_2O} \qquad (5)$$

could not be distinguished, their formation is less likely because (1) aggregation of polar solutes in polar solvents at room temperature is less likely[36] and (2) absorption bands of $\mathrm{(RBr)_3^{\bullet +}}$ and higher oligomers were absent at higher concentrations.

Other possible assignments for this absorption band can be ruled out as follows: (1) The band could not be due to $\mathrm{Br_2^{\bullet -}}$ as this species absorbs at 360 nm and the transient bands observed for various bromo compounds had different λ_{max}; independent studies have shown the absence of free $\mathrm{Br^-}$ in acidic solutions of most bromoalkanes. (2) These bands could not be due to the RBr · Br type of complex[6] as the position of λ_{max} for these complexes is different from that reported here.

Effect of Solute Structure

The transient optical absorption band obtained on pulse radiolysis of O_2-saturated solutions of *n*-alkyl bromides and 1,*m*-dibromoalkanes exhibits properties similar to those of 2σ–$1\sigma^*$ three-electron-bonded species.[24–28] This absorption is attributed to a transition from the uppermost bonding σ to a singly occupied antibonding σ^* level. The strength of this three-electron bond is demonstrated by the optical transition energy (λ_{max}) which directly corresponds to the energy gap between σ and σ^* orbitals. Electron release by the substituent alkyl group (R) can be expected to increase the electron density in the singly occupied antibonding orbital. This would lower the difference between the σ and σ^* levels and the transient absorption would show a red shift. A linear relationship is observed (Fig. 7) when the electron-releasing power of R (Tafts inductive parameter σ^*)[37] is plotted against the optical transition energy ($h\nu$). Despite the scatter, the linear relationship is given by

$$h\nu/\mathrm{eV} = 3.17 + 1.8\sigma^* \qquad \mathrm{(I)}$$

A similar relationship with slope 1.8 was observed for three-electron-bonded species from alkyl iodides.[24] For dimer radical cations of alkyl sulfides, $\mathrm{(R_2S\therefore SR_2)^+}$, the slope was determined to be 1.4.[38] The relative electron-releasing effect by substituents in the case of bromine- and iodine-centred species is greater than with sulfur-centred radical cations although sulfur-centred species carry twice as many electron-releasing groups. This has been explained by their position in the periodic table, which renders these elements electronically 'softer' than sulfur.[24] The lifetimes and the molar absorption coefficient of the transient species formed from bromoalkanes are observed to decrease with increase in the chain length of the alkyl group. These results are similar to those observed for the 2σ–$1\sigma^*$ species obtained from sulfur- and halogen-containing substituents and are explained by the structurally less favoured configuration and the presence of bulky alkyl groups.[24,25,27,37] A theoretical calculation, at least in an approximate level will give a better insight into the strength of two-centre, three-electron bonding which can be correlated with λ_{max} for different radical cations. For intramolecular radical cations, simultaneous steric repulsion and orbital overlapping will indicate the stability rather than the strength of three-electron bonding. We hope to return to this topic in the near future with our theoretical results on alkyl bromides.

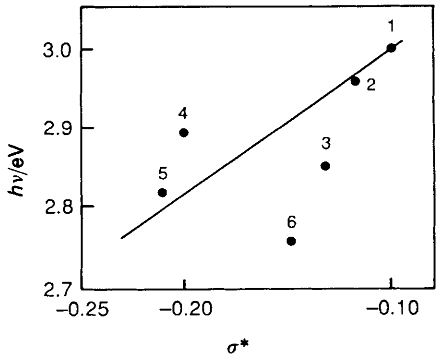
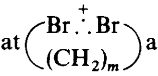


Fig. 7 $h\nu_{max}$/eV as a function of Taft's inductive parameter (σ^*). 1, C_2H_5; 2, C_3H_7; 3, C_4H_9; 4, iso-C_3H_7; 5, sec-C_4H_9 and 6, c-C_6H_{11}

Oxidation Reactions by Radical Cations

The fact that radical cations of bromoalkanes are able to oxidize $\mathrm{Cl^-}$ and other substrates whose redox potentials are quite high, indicates that  $\left(\overset{+}{\mathrm{Br\therefore Br}}\,\mathrm{(CH_2)_m}\right)$ and $\mathrm{(RBr\therefore BrR)^+}$ are strong oxidants. This is also evident from the fact that alkyl bromides could not be oxidized by strong one-electron oxidants such as $\mathrm{Cl_2^{\bullet -}}$, $\mathrm{Tl^{2+}}$. Oxidation reactions with $\mathrm{I^-}$ and promethazine could not be investigated as these species were found to be unstable in strong acidic conditions. From these studies, it may be concluded that the radical cations of alkyl bromides are powerful oxidants with a one-electron oxidation potential of $\geqslant +2.0$ V.

Conclusions

The transient optical absorption bands, formed on the reaction of $^{\bullet}$OH radicals in acidic aqueous solutions of bromoalkanes, are assigned to 2σ–$1\sigma^*$ three-electron-bonded species generated by intra- and inter-molecular association between bromine atoms in 1,*m*-dibromoalkanes and *n*-alkyl bromides, respectively. These cationic species are found to be strong oxidants.

Sincere thanks are due to Dr. R. M. Iyer, Director, Chemistry, Radiochemistry and Isotope Groups, BARC for his keen interest and support for this work.

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Paper 2/04870A; *Received* 10*th September*, 1992