Formation, Stability, and Reactivity of Radical Cations of 1-Bromo-*n*-chloroalkanes in Aqueous Solution: A Pulse Radiolysis Study

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Hydroxyl radicals are able to form solute radical cations in acidic aqueous solutions of 1-bromo-*n*-chloroalkanes ($n = 1-6$). Depending on the value of n, the bromine centered radical cation stabilizes on coordination with an unoxidized bromine atom from another molecule (intermolecular) or with an unoxidized chlorine atom of the same molecule (intramolecular). With $n = 2$, 5, and 6, only dimer radical cations ($\lambda_{max} = 430-450$ nm) are formed through intermolecular coordination whereas, with $n = 1$, 3, and 4, radical cations are stabilized both by intra- and intermolecular coordination, forming intramolecular radical cations ($\lambda_{max} = 380$ nm) or dimer radical cations ($\lambda_{max} = 425-440$ nm) at low and high solute concentrations, respectively. $Cl_2^{\bullet-}$ is unable to undergo an electron transfer reaction with 1-bromo-2-chloroethane whereas $SO_4^{\bullet-}$ is able to react with 1-bromo-2-chloroethane with a bimolecular rate constant of 8.3×10^6 dm^3 mol^{-1} s^{-1}. The dimer radical cation of 1-bromo-2-chloroethane is a strong one-electron oxidant and is able to undergo electron transfer reactions with a number of molecules with high rate constant values (10^9 dm^3 mol^{-1} s^{-1}). The dimer radical cation decays by a deprotonation mechanism, and the stability constant is determined to be 147 dm^3 mol^{-1} at 25 °C. Quantum chemical calculations of the strength of the three-electron bond between two heteroatoms at a semiempirical level with AM1 parametrization show good correlation with experimental results. Good correlation, between experimental results and theoretical calculations, is also observed for variation of the net atomic charge over bromine, the ionization potential (IP) of the molecule, and the difficulty of oxidation of various alkyl halides.

Introduction

Halogenated organic compounds are frequently employed as solvents, pesticides, and refrigerants and for the study of electron transfer reactions in radiation and electrochemical investigations.[1-7] Many of these compounds are hazardous and toxic in nature if metabolized in living species.[7-10] The toxic action of these compounds can be associated with the generation of free radicals. In order to understand the physicochemical properties of halogenated organic compounds, it is necessary to know the identity and reactivity of the transient species generated under different experimental conditions. Such studies are also important, as these compounds are known to play an important role in depletion of tropospheric ozone.[11]

In the past, the identity of transients produced on radiolysis and photolysis of halogenated organic compounds has been determined by optical absorption[12-14] and ESR measurements[15] at 77 K. With the availability of laser flash photolysis and pulse radiolysis techniques, the identity of transients can also be investigated even at room temperature both in organic[3,11,16] and aqueous media.[17-20] The radiolysis of water produces three reactive species (H, OH, e$_{aq}^-$),[21] of which the reaction of OH radical with halogenated organic compounds is most interesting, as it can react by either an addition or an abstraction mechanism.[17-20] Depending upon the pH and the nature of the halogens and substituents, the initially formed OH adduct may either have a lifetime on the microsecond time scale or undergo an abstraction and dehydration reaction.[17-20]

The solute radical cations of alkyl halides undergo deprotonation at low solute concentrations or are converted to dimer radical cations at high solute concentrations.[17,18] The dimer radical cation is characterized by a band in the 400—500 nm region. This band is represented by a $2\sigma-1\sigma^*$ three-electron bond (known as a two-center three-electron or 2c-3e bond) which contains two bonding σ and one antibonding σ^* electrons.[17] Such interactions may take place both by inter- and intramolecular coordination through overlap of p-orbitals.[17] The $2\sigma-1\sigma^*$ three-electron bonding has been observed in organic compounds containing heteroatoms such as S, P, N, O, Br, and I.[22]

The present pulse radiolysis study on 1-bromo-*n*-chloroalkanes is aimed at investigating the possibility of $2\sigma-1\sigma^*$ interaction between bromine and chlorine. Due to a difference in the electronegativities of bromine and chlorine, $2\sigma-1\sigma^*$ bonded species may be formed only if additional stability could be introduced by the geometrically favored structure of the transient. The experimental results on the formation of 2c-3e bonded species on OH radical induced reaction with 1-bromo-*n*-chloroalkanes in aqueous solutions are reported in this paper. A quantum chemical computation has been performed to find the structures of a series of 1-bromo-*n*-chloroalkanes and their respective radical cations. The inter- (Br∴Br) and intra-(Br∴Cl) molecular two-center three-electron (2c-3e) bond strengths have also been determined. The computed bond order between two Br atoms making an intermolecular 2c-3e bond and that between Br and Cl atoms making an intramolecular 2c-3e bond are also presented.

Experimental Section

Preparation of Solution. The details of the chemicals used are as follows: Bromochloromethane (purum, Fluka), 1-bromo-

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2-chloroethane (purity 98%, Aldrich), 1-bromo-3-chloropropane (purum, Fluka), and 1-bromo-6-chlorohexane (purity 97%, Aldrich) were used without any further purification. 1-Bromo-4-chlorobutane and 1-bromo-5-chloropentane were synthesized in the laboratory using the detailed procedures below.

Preparation of 1-Bromo-4-chlorobutane. To a magnetically stirred mixture of dry THF (25 g, 0.35 mol) and anhydrous $ZnCl_2$, acetyl chloride (30 mL, 0.35 mol) was added dropwise. After the immediate exothermic reaction subsided, the mixture was refluxed for 1.5 h and the content of the flask distilled directly under reduced pressure to afford pure 1-acetoxy-4-chlorobutane. Yield: 35.8 g (68.6%). Bp: 90−92 °C/20 Torr. IR: 1730 and 1240 cm^{-1}. ^{1}H NMR: δ 1.4−1.8 (m, 4H), 2.1 (s, 3H), 3.48 (t, J = 7 Hz, 2H), 4.12 (t, J = 7 Hz, 2H).

The above compound (13.0 g) was dissolved in methanol (50 mL) containing *p*-toluenesulphonic acid (0.2 g) and refluxed for 4 h. Most of the solvent was removed by distillation at atmospheric pressure, the residue treated with $NaHCO_3$(s) (5.0 g), and the mixture extracted with solvent ether (3 × 40 mL). The combined ether extracts were concentrated in a water bath, and the residue was distilled under reduced pressure to furnish 4-chlorobutanol. Yield: 8.0 g (85.4%). Bp: 110 °C/25 Torr. IR: 3440, 1430, and 1060 cm^{-1}. ^{1}H NMR: δ 1.3−1.9 (m, 4H), 2.41 (br s, D_2O exchangeable, ^{1}H), 3.48 (t, J = 7 Hz, 2H), 3.67 (t, J = 7 Hz, 2H).

To a stirred and cooled (0 °C) mixture of the above alcohol (4.0 g, 0.036 mol) and pyridine (1.0 mL) was injected PBr_3 (1.5 mL). Stirring was continued for 1 h at 0 °C and 3 h at room temperature. It was diluted with ice-cold water and extracted with solvent ether (3 × 30 mL). The ether layer was washed with water, aqueous dilute HCl (2 N), water, and finally brine. After drying and solvent removal, the residue was distilled to give 1-bromo-4-chlorobutane, which was further purified by repeated (four times) distillation. Yield: 2.8 g (44%). Bp: 90 °C/20 Torr. IR: 1430 and 1180 cm^{-1}. ^{1}H NMR: δ 1.3−1.9 (m, 4H), 3.48 (t, J = 7 Hz, 2H), 3.54 (t, J = 7 Hz, 2H).
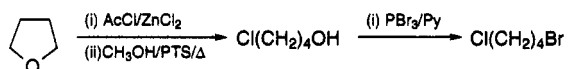
Preparation of 1-Bromo-5-chloropentane. Pentane-1,5-diol (15.11 g) was converted to 5-bromopentanol following a reported procedure.[23] Yield: 20.0 g (82.5%). Bp: 76 °C/30 Torr. IR: 3380, 1440, and 1060 cm^{-1}. ^{1}H NMR: δ 1.2−1.7 (m, 6H), 2.78 (br s, D_2O exchangeable, 1H), 3.54 (t, J = 7 Hz, 2H), 3.68 (t, J = 7 Hz, 2H).

To a cooled (0 °C) and stirred mixture of the above alcohol (8.0 g, 0.05 mol) and triethylamine (13.9 mL, 0.1 mol) in dry CH_2Cl_2 (30 mL) was added methanesulphonyl chloride (5.8 mL, 0.075 mol) over 0.5 h. After 3 h, it was poured into ice−water, the organic layer separated, and the aqueous portion extracted with $CHCl_3$ (2 × 40 mL). The combined organic extract was successively washed with water, aqueous $NaHCO_3$ (10%), water, aqueous dilute HCl (2 N), water, and brine and finally dried. After the solvent was removed in vacuo, the crude product (8.0 g) was dissolved in acetone (60 mL), LiCl(s) (3.0 g) was added, and the mixture was refluxed for 48 h. After the mixture was cooled to room temperature, it was concentrated in vacuo, diluted with water, and extracted with ether (3 × 50 mL). The ether extract was washed with water and brine and dried. Removal of solvent at atmospheric pressure followed by repeated (four times) distillation under Ar gave 1-bromo-5-chloropentane. Yield: 3.62 g (58.3%). Bp: 70 °C/10 Torr.

IR: 1430 and 1180 cm^{-1}. ^{1}H NMR: δ 1.2−1.8 (m, 6H), 3.42 (t, J = 7 Hz, 2H), 3.56 (t, J = 7 Hz, 2H).
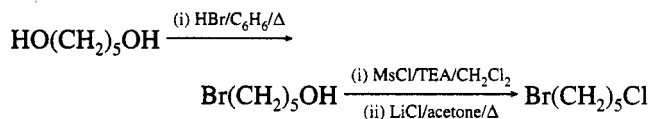
All other chemicals used were of 'analar' grade purity. The solutions were prepared in deionized 'nanopure' water, and fresh solutions were used for each experiment. Iolar grade (Indian Oxygen) N_2O, N_2, and O_2 gases were used for purging the solutions. Each rate constant value is the average of at least three independent experiments, and the values are within ±15% error.

Irradiation Procedure. Pulse radiolysis studies have been carried out with 7 MeV electron pulses of 50 ns pulse width, obtained from a linear accelerator, whose details are described elsewhere.[24] An aerated aqueous solution of KSCN (10 m mol dm^{-3}) was used for measuring the dose delivered per pulse, taking Gϵ = 21 520 dm^3 mol^{-1} cm^{-1} per 100 eV at 500 nm for the transient (SCN)$_2^-$ species.[25] The dose delivered per pulse was 16 Gy (1 Gy = 1 J Kg^{-1}). The reaction of OH radicals in acidic solution was carried out under O_2-saturated conditions to scavenge H and e$_{aq}^-$ (e$_{aq}^-$ + H$^+$ → H + H_2O; H + O_2 → HO_2).

Stability of Solution. The stability of the bromochloroalkanes in the presence of a high acid concentration was investigated by monitoring the formation of Br$^-$/Cl$^-$ spectrophotometrically,[26] and they were observed to be quite stable under the experimental conditions.

Calculations. Quantum chemical calculations have been carried out at the semiempirical level with AM1 parametrization,[27] adopting a standard conjugate gradient technique to find out the structures of different bromochloroalkanes in their fully optimized geometries. A complete search has been performed to find out the geometries of the most stable conformers of different bromochloroalkanes, and the net atomic charge over the bromine atom in different systems has been calculated following the method of Mulliken's population analysis under the RHF framework. The structures of the radical cations of the 1-bromo-*n*-chloroalkanes and those of the respective dimer radical cations are computed under the UHF/AM1 framework. The 2c-3e bond energy between the oxidized bromine and the unoxidized one in dimer radical cations of 1-bromo-*n*-chloroalkanes has been computed from the difference in the total energy of this dimer at its most stable geometry and at the dissociation limit along the Br−Br distance path. The 2c-3e bond energy between the oxidized Br atom and the Cl atom of the same radical cation for 1-bromo-*n*-chloroalkanes has been computed from the difference in energy of the most stable structure when Br and Cl are close enough to form this bond and the structure where Br and Cl are too far off to make any such bond.[28]

Results

Bromochloromethane. Figure 1 shows the transient optical absorption spectrum obtained on pulse radiolysis of an O_2-saturated aqueous solution of bromochloromethane (1.0 × 10^{-2}, [HClO$_4$] = 1.0 mol dm^{-3}). It exhibits very little absorption in the 300−600 nm region. Pulse radiolysis of an N_2O-saturated neutral aqueous solution of bromochloromethane (1.0 × 10^{-3} mol dm^{-3}) also does not show appreciable absorption in the same region. However, when [HClO$_4$] is increased, a broad transient absorption band starts appearing in the 380−480 nm region. Figure 2a shows the variation in the absorbance of the
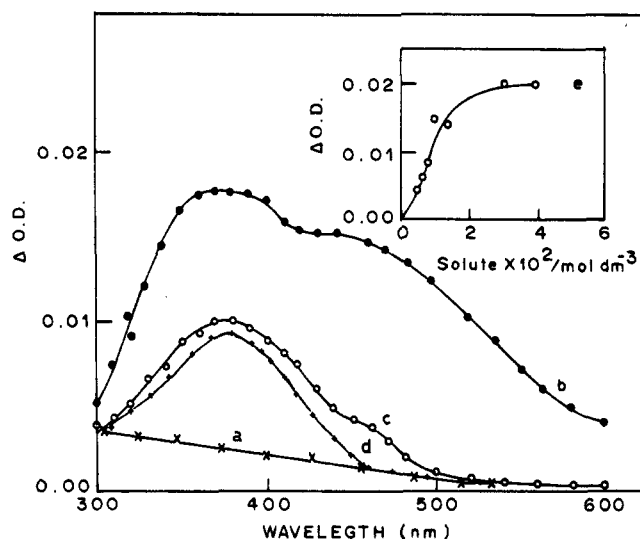
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Figure 1. Transient optical absorption spectrum obtained on pulse radiolysis of an aqueous solution of bromochloromethane (BCM): (a) [BCM] = 1.0×10^{-2} mol dm^{-3}, [HClO$_4$] = 1.0 mol dm^{-3}; (b) [BCM] = 1.0×10^{-2} mol dm^{-3}, [HClO$_4$] = 11.9 mol dm^{-3}; (c) [BCM] = 2.0 $\times$ 10^{-3} mol dm^{-3}, [HClO$_4$] = 11.9 mol dm^{-3}; (d) [BCM] = 1.0 $\times$ 10^{-4} mol dm^{-3}, [HClO$_4$] = 11.9 mol dm^{-3}; (e) variation of absorbance as a function of solute (BCM) concentration (λ = 440 nm, [HClO$_4$] = 11.9 mol dm^{-3}).
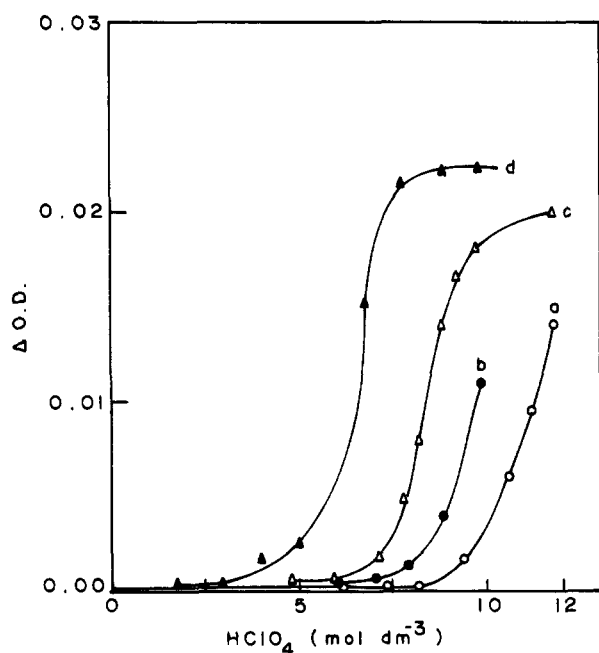

Figure 2. Variation of optical absorbance as a function of [HClO$_4$]: (a) bromochloromethane (1.5 $\times$ 10^{-2} mol dm^{-3}, λ = 420 nm); (b) dibromomethane (1.2 $\times$ 10^{-2} mol dm^{-3}, λ = 410 nm); (c) 1-bromo-2-chloroethane (1.2 $\times$ 10^{-2} mol dm^{-3}, λ = 420 nm); (d) 1-bromo-3-chloropropane (1.1 $\times$ 10^{-3} mol dm^{-3}, λ = 385 nm).

transient band (420 nm), formed on pulse radiolysis of bromo-chloromethane (1.5 $\times$ 10^{-2} mol dm^{-3}), as a function of [HClO$_4$]. The absorbance starts appearing only when [HClO$_4$] > 8.0 dm^{-3} and does not reach the saturation value even when [HClO$_4$] = 11.9 mol dm^{-3}.

Figure 1b shows the transient optical absorption spectrum obtained on pulse radiolysis of an aerated aqueous solution of bromochloromethane (1.0 $\times$ 10^{-2} mol dm^{-3}, [HClO$_4$] = 11.9 mol dm^{-3}). It exhibits an absorption band in the 380 nm region and a broad shoulder in the 420—460 nm region. The decay at 380 and 440 nm was of a different nature, suggesting the presence of two different species. When the solute concentration
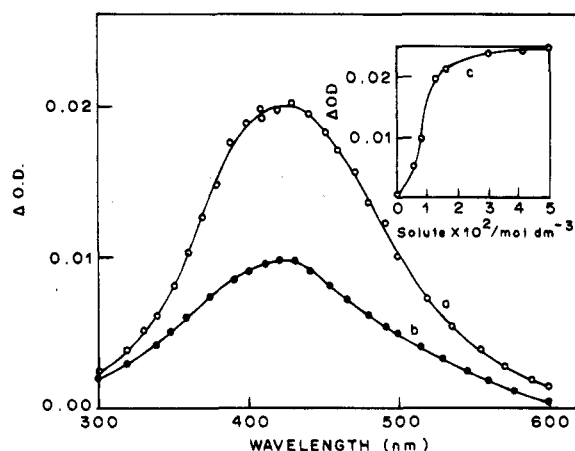

Figure 3. Transient optical absorption spectrum obtained on pulse radiolysis of an O$_2$-saturated aqueous solution of 1-bromo-2-chloroethane: (a) 1.3 $\times$ 10^{-2} mol dm^{-3}, [HClO$_4$] = 9.8 mol dm^{-3}; (b) 7.3 $\times$ 10^{-3} mol dm^{-3}, [HClO$_4$] = 9.8 mol dm^{-3}; (c) variation of absorbance (420 nm) as a function of solute concentration ([HClO$_4$] = 9.8 mol dm^{-3}).

is reduced to 2.0×10^{-3} mol dm^{-3}, the absorption in the 420—460 nm region reduced appreciably while the decrease at 380 nm was much less (Figure 1c). It also suggests the presence of two different species. Figure 1d shows the transient optical absorption spectrum on pulse radiolysis of an O$_2$-saturated aqueous solution of bromochloromethane (1.0 $\times$ 10^{-4} mol dm^{-3}, [HClO$_4$] = 11.9 mol dm^{-3}), which exhibits a band with λ_{max} = 380 nm. This band was observed to grow by first-order kinetics; the first-order rate constant (k_{obs}) increased linearly with solute concentration (1.0—4.0) $\times$ 10^{-4} mol dm^{-3}. The bimolecular rate constant determined from the slope of a linear plot of k_{obs} vs solute concentration was 2.5 $\times$ 10^9 dm^3 mol^{-1} s^{-1}. The band was observed to decay by first-order kinetics with $t_{1/2}$ = 7.5 μs. Figure 1e shows the variation in the absorbance at 440 nm as a function of solute concentration. The absorbance increases, reaching a plateau value at 4.0 $\times$ 10^{-2} mol dm^{-3}.

1-Bromo-2-chloroethane. Figure 3a shows the transient optical absorption spectrum obtained on pulse radiolysis of an O$_2$-saturated aqueous solution of 1-bromo-2-chloroethane (1.3 $\times$ 10^{-2} mol dm^{-3}, [HClO$_4$] = 9.8 mol dm^{-3}). The band (λ_{max} = 430 nm) was observed to decay by first-order kinetics with $t_{1/2}$ = 5.9 μs. The intensity and the lifetime of this band were found to decrease with a decrease in solute concentration without any change in the nature of the transient spectrum (Figure 3b). The intensity was also found to increase with [HClO$_4$] and appeared only when [HClO$_4$] was >5.0 mol dm^{-3} (Figure 2c). The bimolecular rate constant for the buildup of this band was determined to be 4.5 $\times$ 10^9 dm^3 mol^{-1} s^{-1}.

1-Bromo-3-chloropropane. Figure 4a shows the transient optical absorption spectrum obtained on pulse radiolysis of an aerated aqueous solution of 1-bromo-3-chloropropane (2.0 $\times$ 10^{-3} mol dm^{-3}), which exhibits a broad absorption band with λ_{max} = 380 nm. It decayed by first-order kinetics with $t_{1/2}$ = 9.7 μs. As the concentration of the solute is increased [(2.0—8.0) $\times$ 10^{-3} mol dm^{-3}], there is very little change in the nature of the transient spectrum. At 2.0 $\times$ 10^{-2} mol dm^{-3} solute concentration, the transient optical absorption spectrum (Figure 4b) shows a broad band with λ_{max} = 390 nm and an increased absorption in the 400—550 nm region. This suggests the presence of another transient species, in addition to that observed in Figure 4a. The difference of these spectra exhibits a broad band of small intensity at λ_{max} = 440 nm (Figure 4c). The intensity of the transient band (380 nm) was nearly constant with solute concentration [(2.0—8.0) $\times$ 10^{-3} mol dm^{-3}]. The
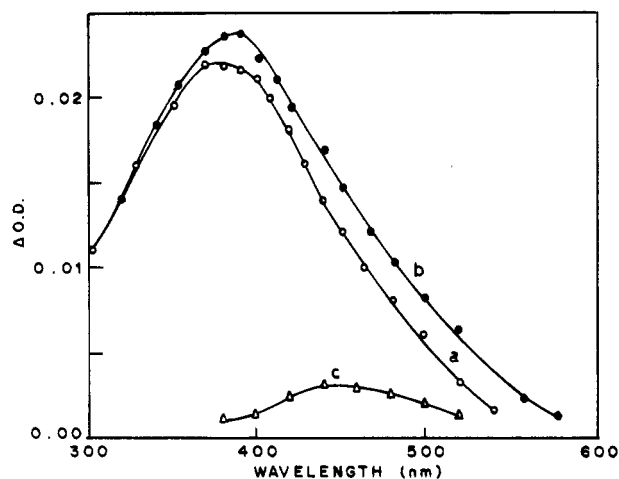
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Figure 4. Transient optical absorption spectrum obtained on pulse radiolysis of an O_2-saturated aqueous solution of 1-bromo-3-chloropropane: (a) 2.0×10^{-3} mol dm^{-3}, $[HClO_4] = 7.8$ mol dm^{-3}; (b) 2.0×10^{-2} mol dm^{-3}, $[HClO_4] = 7.8$ mol dm^{-3}; (c) difference of parts a and b.
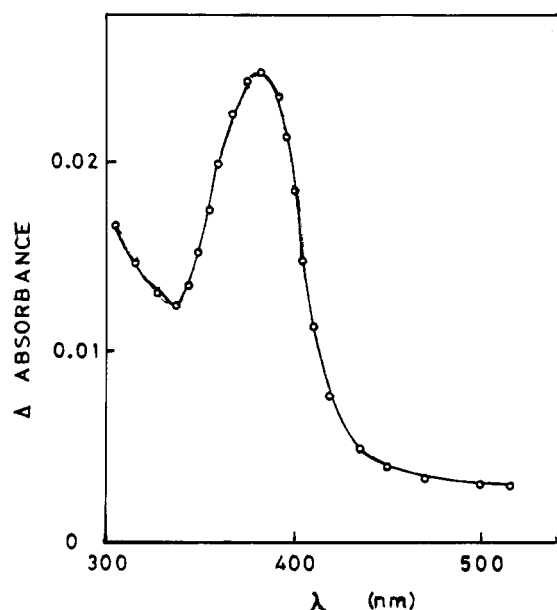

Figure 5. Transient optical absorption spectrum obtained on pulse radiolysis of an O_2-saturated solution of 1-bromo-4-chlorobutane (8.7 $\times 10^{-3}$ mol dm^{-3}, $[HClO_4] = 7.8$ mol dm^{-3}, dose $= 1.1 \times 10^{17}$ eV cm^{-3}).

increased absorption at higher wavelengths appeared only at high solute concentrations.

1-Bromo-4-chlorobutane. Figure 5 shows the transient optical absorption spectrum obtained on pulse radiolysis of an O_2-saturated aqueous solution of 1-bromo-4-chlorobutane (8.7 $\times 10^{-3}$ mol dm^{-3}, $[HClO_4] = 7.8$ mol dm^{-3}), 3.5 μs after the pulse. It exhibits an absorption band with $\lambda_{max} = 380$ nm. The band was observed to decay by first-order kinetics with $t_{1/2} = 9.3$ μs. Its intensity remained nearly constant at low solute concentrations (4−8) $\times 10^{-3}$ mol dm^{-3}. The absorbance in the 400−500 nm region was found to increase at higher solute concentrations; however, distinct peak could not be observed.

1-Bromo-n-chloroalkanes (n = 5 and 6). Similar studies have been carried out for higher 1-bromo-n-chloroalkanes (n = 5 and 6). In all these cases (Figure 6), the intensity of the transient optical absorption band was observed to increase with solute concentration. The position of λ_{max} is as shown in Table 1. Due to the low intensity of the optical absorption, $t_{1/2}$ and the bimolecular rate constant values could not be determined
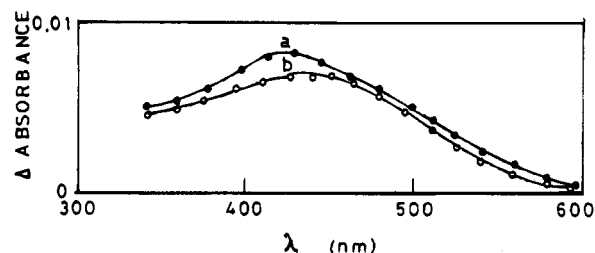

Figure 6. Transient optical absorption spectrum obtained on pulse radiolysis of an O_2-saturated aqueous solution of (a) 1-bromo-5-chloropentane and (b) 1-bromo-6-chlorohexane.

with accuracy and are not included in Table 1. With $n = 2, 5$, and 6, only one transient optical absorption was observed. Gϵ values, for these 1-bromo-n-chloroalkanes, are determined under identical conditions of dose, solute, and $HClO_4$ concentration. The values are observed to decrease with increasing methylene chain length.

Redox Studies. The transient decay of $Cl_2^{\bullet-}$, formed on pulse radiolysis of an aerated aqueous solution of Cl^- (2.0 $\times 10^{-2}$ mol dm^{-3}, pH = 1.0, $\lambda = 340$ nm), remained unaffected in the presence of a low concentration of 1-bromo-2-chloroethane (5.0 $\times 10^{-4}$ mol dm^{-3}), suggesting that $Cl_2^{\bullet-}$ is not able to oxidize 1-bromo-2-chloroethane. The $SO_4^{\bullet-}$ radical anion is a strong one-electron oxidant.[29] The decay of $SO_4^{\bullet-}$, formed on pulse radiolysis of an N_2-saturated aqueous solution of $S_2O_8^{-2}$ (2 $\times 10^{-2}$ mol dm^{-3}, pH = 6.0, [*tert*-butyl alcohol] 0.2 mol dm^{-3}, $\lambda = 460$ nm), was found to become faster on addition of 1-bromo-2-chloroethane (1−5) $\times 10^{-3}$ mol dm^{-3}. The bimolecular rate constant for this reaction was determined to be 8.3 $\times 10^6$ dm^3, mol^{-1} s^{-1}. Time-resolved studies do not show the formation of a new band with the decay of the 460 nm band of $SO_4^{\bullet-}$. Although the solute radical cation formed on electron transfer at neutral pH is expected to be unstable and may undergo a deprotonation reaction, the low bimolecular rate constant value may also suggest that the reaction between $SO_4^{\bullet-}$ and the solute is by H abstraction.[30] In order to resolve these two processes (electron transfer and H atom abstraction), pulse radiolysis studies were carried out in D_2O and the decay of the 460 nm band of $SO_4^{\bullet-}$ was monitored for various concentrations of 1-bromo-2-chloroethane (1−5) $\times 10^{-3}$ mol dm^{-3}. The bimolecular rate constant was determined to be 7.2 $\times 10^6$ dm^3 mol^{-1} s^{-1}. The closeness of the rate constant values in two different solvents (H_2O and D_2O) suggests that the reaction of $SO_4^{\bullet-}$ with 1-bromo-2-chloroethane is by an electron transfer process and not by H abstraction. From these studies it appears that the redox potential value of the $ClC_2H_4Br^+/ClC_2H_4Br$ couple is more than 2.1 V. The solute radical cation should therefore be a strong one-electron oxidant. It should be able to oxidize compounds having a redox potential value lower than 2.1 V. The transient band formed on pulse radiolysis of an O_2-saturated solution of 1-bromo-2-chloroethane (1.2 $\times 10^{-2}$ mol dm^{-3}, $[HClO_4] = 7.8$ mol dm^{-3}, $\lambda = 430$ nm) was observed to decay faster in the presence of low concentrations of SCN^- [(0.2−1.4) $\times 10^{-4}$ mol dm^{-3}]. The bimolecular rate constant determined from the slope of the linear plot of k_{obs} vs SCN^- concentration was 2.7 $\times 10^9$ dm^3 mol^{-1} s^{-1}. Similarly, the decay was also observed to become faster in the presence of small concentrations of Cl^- [(1−8) $\times 10^{-3}$ mol dm^{-3}], and the bimolecular rate constant was determined to be 2.9 $\times 10^8$ dm^3 mol^{-1} s^{-1}.

Discussion

Effect of Solute Concentration. The transient optical absorption spectra obtained on pulse radiolysis of bromochlo-

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TABLE 1: Physical Properties of the Transients Formed on Pulse Radiolysis of O_2-Saturated Solutions of 1-Bromo-n-chloroalkanes

n for Br(CH)$_n$Cl	λ_{max} (nm)	$t_{1/2}$ (μs)	Gϵ (dm^3 mol^{-1} cm^{-1})	formation rate constant (dm^3 mol^{-1} s^{-1})	transient species
1	380	7.5		2.5×10^9	$\left[\begin{smallmatrix} Br\therefore Cl \\ (CH_2) \end{smallmatrix}\right]^+$
	425	8.8			[Br∴Br]$^+$
2	430	5.9	14.3×10^3	4.5×10^9	[Br∴Br]$^+$
3	380	9.7		2.0×10^9	$\left[\begin{smallmatrix} Br\therefore Cl \\ (CH_2)_3 \end{smallmatrix}\right]^+$
	440				[Br∴Br]$^+$
4	380	9.3			$\left[\begin{smallmatrix} Br\therefore Cl \\ (CH_2)_4 \end{smallmatrix}\right]^+$
	440				[Br∴Br]$^+$
5	440		7.2×10^2		[Br∴Br]$^+$
6	450		6.1×10^2		[Br∴Br]$^+$

romethane (Figure 1), 1-bromo-3-chloropropane (Figure 4), and 1-bromo-4-chlorobutane (Figure 5) showed the formation of two absorption bands. The transient optical absorption band in the low-wavelength region was present for low solute concentrations, and its intensity remained nearly constant at low solute concentrations. Therefore, it should be due to a monomeric species. The transient band in the higher wavelength region appeared only at higher solute concentrations, and its intensity was observed to depend strongly on solute concentration. Therefore, it could be due to a dimeric species. At higher solute concentrations, the increase in the absorbance in the higher wavelength region for the solute with $n = 3$ and 4 was smaller as compared to the increase in the absorbance observed for the solute with $n = 1$. This suggests that the monomeric species with $n = 3$ and 4 are very stable and the amount of the corresponding dimeric species formed is very small. This is expected because the five- and six-membered ring configurations formed on p-orbital overlap of bromine and chlorine atoms (intramolecularly) in the case of the radical cations of 1-bromo-3-chloropropane and 1-bromo-4-chlorobutane are the most stable structures due to less steric hindrance.[22] In the case of other 1-bromo-n-chloroalkanes ($n = 2$, 5, 6) only one transient absorption band was observed and, as the intensity of the transient band increased with solute concentration, the absorption band has been assigned to the dimeric species.

Site of Attack. Earlier pulse radiolysis studies on n-alkyl bromides and 1,m-dibromoalkanes have shown the formation of inter- and intramolecular radical cations, suggesting oxidation at bromine. Therefore, in the present case of bromochloroalkanes, OH radical attack should also be at the bromine atom. In order to further confirm this, pulse radiolysis studies were carried out on 1-chloropropane, under the identical experimental conditions employed for 1-bromo-3-chloropropane, and the transient optical absorption band was not observed. This shows that the site of OH radical attack is at the bromine center and not at chlorine.

Assignment of Transient Bands. The primary reactive species produced on pulse radiolysis of O_2-saturated acidic aqueous solutions are OH and HO$_2$ radicals. Therefore, it is important to know the contribution of these radicals toward the formation of the transient bands of 1-bromo-n-chloroalkanes. In the presence of *tert*-butyl alcohol, an efficient OH radical scavenger, the transient optical absorption bands were not observed. This suggests that the transient bands are due to reaction of OH radicals with the solute, as HO$_2$ radicals would still be produced in high yield. In N$_2$-saturated solutions, where HO$_2$ radicals would not be produced, pulse radiolysis studies

showed the formation of transient bands similar to those observed in O$_2$-saturated solutions. This also suggests that the bands are due to reaction of OH radicals with the solute. Moreover, HO$_2$ radical is a mild oxidizing agent with a redox potential value of 1.0 V.[31] Stronger oxidizing agents such as Cl$_2^-$ ($E° = 2.1$ V) failed to form the transient bands (see above). This shows that HO$_2$ radical could not undergo electron transfer reaction with 1-bromo-n-chloroalkanes. Therefore, it can be concluded that the observed bands are due to reaction of OH radicals with bromochloroalkanes.

It is reported[32] that pulse radiolysis of deaerated aqueous solutions containing high concentrations of HClO$_4$ shows a transient band with $\lambda_{max} = 335$ nm. This band is assigned to ClO$_4$ radical formed on reaction of H/OH radicals with ClO$_4^-$. The intensity of this band would decrease in aerated solutions due to scavenging of H atoms. It is also reported[32] that, owing to competitive processes, the formation of ClO$_4$ radical would be reduced in the presence of solute. Therefore, under our experimental conditions, the observed band could not be due to ClO$_4$ radicals. Pulse radiolysis of O$_2$-saturated 7.8 mol dm^{-3} HClO$_4$ has shown a very small absorption above 360 nm. Therefore, the absorption bands (Figure 1−6) could not be due to any radiolysis product of HClO$_4$. The reaction of ClO$_4$ radicals with the solute was indirectly studied on pulse radiolysis of an O$_2$-saturated neutral aqueous solution of NaClO$_4$ (8.1 mol dm^{-3}) in the presence of 1-bromo-3-chloropropane (2.5 × 10^{-3} mol dm^{-3}). The transient optical absorption spectrum showed very little absorption above 360 nm. Therefore, ClO$_4$ radical does not react with 1-bromo-3-chloropropane to form the transient bands, as observed in Figure 4. The formation of these bands required high H$^+$ concentrations (Figure 1−6).

From these studies it can be concluded that the transient optical absorption bands observed for different 1-bromo-n-chloroalkanes are due to reaction of OH radicals, in the presence of high H$^+$ concentrations. Additional evidence in support of this conclusion came from pulse radiolysis studies carried out in H$_2$SO$_4$ instead of HClO$_4$. The nature of the transient optical absorption spectrum obtained on pulse radiolysis of an O$_2$-saturated aqueous solution of 1-bromo-2-chloroethane (1.2 × 10^{-2} mol dm^{-3}) in 10 mol dm^{-3} H$_2$SO$_4$ was similar to that obtained in HClO$_4$ (see Figure 3a) with λ_{max} at 430 nm. The decay kinetics was also similar to that observed in HClO$_4$. Figure 7 displays the variation of absorbance ($\lambda = 430$ nm) as a function of Hammett acidity function (H_0).[33] It is seen from the figure that the variation of absorbance gives a similar profile irrespective of the nature of the acid used. As the Hammett acidity function is not available for higher acid concentrations
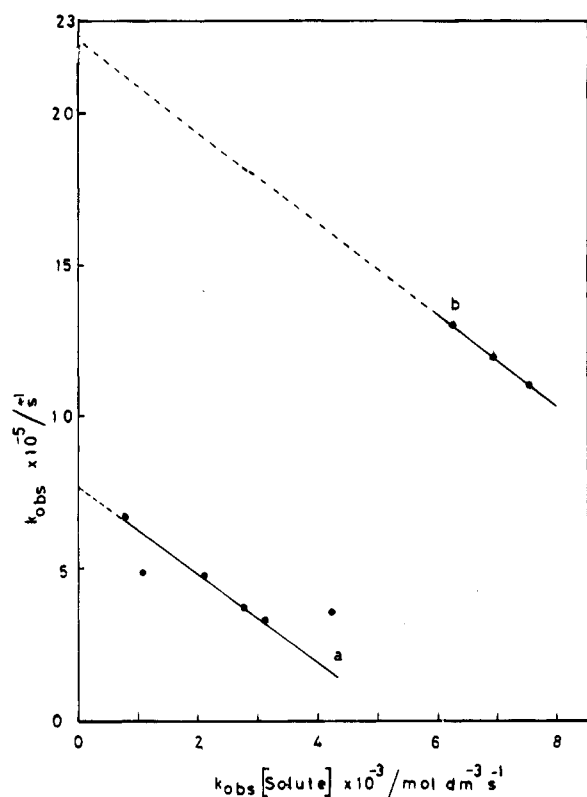
Figure 7. Variation of transient optical absorbance obtained on pulse radiolysis of an O_2-saturated aqueous solution of 1-bromo-2-chloroethane (1.2×10^{-2} mol dm^{-3}, $\lambda_{max} = 430$ nm) as a function of Hammett acidity function (H_0) in the presence of (●) H_2SO_4 and (○) $HClO_4$.

SCHEME 1

(>10 mol dm^{-3}), the data plotted are restricted to the corresponding H_0 values available. The absorbance of the 430 nm band in 10 mol dm^{-3} H_2SO_4 was lower than that observed in 10 mol dm^{-3} $HClO_4$ at the same solute (1-bromo-2-chloroethane) concentration. This is because the H_0 value of $HClO_4$ is higher compared to that of H_2SO_4 at this concentration. Similar results were also observed for other 1-bromo-n-chloroalkanes in H_2SO_4. From these results, one can safely conclude that the transient optical absorption bands observed for 1-bromo-n-chloroalkanes in $HClO_4$ are due to the reaction of OH radicals in the presence of high H$^+$ concentrations and not due to the reaction of radicals derived on the radiolysis of $HClO_4$ with 1-bromo-n-chloroalkanes. Similar observations with substituted alkyl sulfides are reported in literature.[34]

Pulse radiolysis of neutral N_2O-saturated aqueous solutions of 1-bromo-n-chloroalkanes failed to give any transient optical absorption band in the 300—600 nm region, suggesting that the OH adduct if formed must be highly unstable. It may decay by an H atom abstraction mechanism.[20] The OH radical induced acid-catalyzed oxidation of a number of organic compounds is known to take place in the pH range 1—3.[17,18,35,36] Therefore, it is possible that acid-catalyzed oxidation of 1-bromo-n-chloroalkanes may also be taking place in the present case and the OH adduct is converted to solute radical cation (Scheme 1). Pulse radiolysis of dilute aerated acidic solutions of alkyl bromides (1.0×10^{-4} mol dm^{-4}) does not show any transient optical absorption band in the 350—550 nm region. The solute radical cations of alkyl bromides are not stable and may decay by a deprotonation mechanism. The transient optical absorption band (380 nm) formed on pulse radiolysis of a dilute acidic aqueous solution of bromochloromethane, 1-bromo-3-chloropropane, and 1-bromo-4-chlorobutane could not be due to a simple solute radical cation. It is well-known[22] that solute radical cations of aliphatic compounds containing a heteroatom have a high tendency to stabilize on coordination with free a p-orbital of another heteroatom. Therefore, the transient optical absorption spectrum obtained on pulse radiolysis of an acidic

aqueous solution of bromochloromethane, 1-bromo-3-chloropropane, and 1-bromo-4-chlorobutane could be due to an intramolecular radical cation formed on p-orbital overlap of oxidized bromine with the p-orbital of the chlorine atom.

Similarly the transient optical absorption band observed at high solute concentrations should be due to intermolecular dimer radical cation formed on p-orbital overlap of oxidized bromine with the free p-orbital of the bromine of the second molecule.

Effect of HClO₄ Concentration. The intensities of transient bands formed on reaction of OH radicals with 1-bromo-n-chloroalkanes in the presence of $HClO_4$ were observed to increase with [$HClO_4$], reaching a saturation value above 8.0 mol dm^{-3} (for $n > 3$). For $n < 3$, the saturation value was not observed even at 11.8 mol dm^{-3} $HClO_4$. This may not represent a true variation of intensity with H$^+$, as the yield of OH radicals is expected to decrease with increasing concentration of $HClO_4$. A part of the radiation energy would be absorbed by $HClO_4$, and the yield of OH radicals would decrease with increasing concentration of $HClO_4$. As the concentration of the acid is increased, more of the OH adduct is reacted with H$^+$ to form the solute radical cation. Due to the lack of knowledge on the exact fraction of radiation energy absorbed by water in strongly acidic solutions of 1-bromo-n-chloroalkanes, the yields and the extinction coefficients of the transient bands could not be estimated.

Decay Kinetics. Only one transient optical absorption band was observed when $n = 2, 5$, and 6, and with $n = 5$ and 6, the intensity of the absorption band was very small. The detailed decay kinetic studies were therefore carried out with 1-bromo-2-chloroethane. The transient band ($\lambda = 430$ nm) was found to decay by first-order kinetics with a lifetime dependent on the solute and $HClO_4$ concentration. The band appeared only when the concentration of $HClO_4$ was more than 5.0 mol dm^{-3} even at high solute concentrations. Therefore, at lower $HClO_4$ concentrations, the OH adduct may be decaying by reaction 2 (Scheme 1). At higher concentrations of $HClO_4$, the OH adduct may be converted to solute radical cation (reaction 3), which is further converted to dimer radical cation via equilibrium 4. Asmus et al.[37] have shown that the rate-determining step for the decay of dimer radical cations of alkyl sulfides can be either by the decay of the back reaction of the equilibrium (k_{-4}) or by the deprotonation of the solute radical cation (k_5). Using different concentrations of proton acceptor to accelerate the deprotonation reaction of solute radical cations of alkyl sulfides, they have shown from the plots of k_{obs} vs k_{obs}[solute] that the deprotonation would be the rate-determining step if the plots had the same slope (k_4) and different intercepts (k_5 + deprotonation rate constant × [proton acceptor]). The decay by the back reaction of the equilibrium would give the same intercept (k_{-4}) and different slopes $k_4/(k_5$ + deprotonation rate constant × [proton acceptor]). This method of analysis for the entire decay scheme is not possible in the present case, as the dimer radical cations are observed only at high $HClO_4$ concentrations and variation of k_{obs} for different concentrations of proton acceptor could not be carried out. However, it has been shown, from the plot of k_{obs} vs k_{obs}[solute] for different acid concentrations, that the deprotonation of solute radical cation would be the rate-determining step if the plots had the same slope and different intercepts.[18,37] Figure 8 shows a plot of k_{obs} vs k_{obs}[ClC$_2$H$_4$Br] for 9.8 and 8.8 mol dm^{-3} $HClO_4$. From this figure it is clear that the decay is by a deprotonation mechanism and the stability constant of the dimer radical cation is equal to the slope of the line (147 dm^3 mol^{-1}). From the formation rate constant value of 4.5×10^9 dm^3 mol^{-1} s^{-1}, k_{-3} is calculated to be 3.1×10^7 s^{-1}.

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Figure 8. Plot of k_{obs} vs $k_{obs}[ClC_2H_4Br]$ for [HClO$_4$] of (a) 9.8 and (b) 8.8 mol dm^{-3}.

TABLE 2: Variation of Net Atomic Charge over the Halogen Atom and IP in Different Alkyl Halides of Their Most Stable Conformer[a]

	atomic charge on halogen atom with asterisk (au)				
n	H(CH$_2$)$_n$Cl*	H(CH$_2$)$_n$Br*	Br(CH$_2$)$_n$Br*	Cl(CH$_2$)$_n$Br*	H(CH$_2$)$_n$I*
1	−0.117	−0.039		−0.001	0.058
	(11.338)	(10.803)	(10.958)	(11.086)	(10.513)
2	−0.129	−0.054	−0.034	−0.031	0.045
	(11.153)	(10.692)	(11.014)	(11.034)	(10.429)
3	−0.127	−0.055	−0.036	−0.035	0.046
	(11.134)	(10.689)	(10.885)	(10.918)	(10.429)
4	−0.127	−0.054	−0.044	−0.044	0.046
	(11.133)	(10.630)	(10.836)	(10.851)	(10.428)
5	−0.127	−0.052	−0.046	−0.046	0.046
	(11.134)	(10.688)	(10.801)	(10.806)	(10.427)

[a] The values shown in parentheses are the ionization potential (IP) of the respective molecule in eV.

TABLE 3: Computed Properties of Two-Center Three-Electron Bond in Dimer Radical Cations of 1-Bromo-*n*-chloroalkanes

n for [Cl(CH$_2$)$_n$Br]$_2$•$^+$	bond dissociation energy (kcal/mol)	bond distance (Br−Br, Å)	$\langle S_z^2 \rangle$	charge over Br (au)	bond order (Br−Br)
1	43.44	2.32	0.75	0.15	0.50
2	46.96	2.32	0.75	0.23	0.50
3	58.74	2.34	0.75	0.21	0.50
4	54.81	2.34	0.75	0.17	0.50
5	48.29	2.32	0.75	0.09	0.50

The dimer radical cations of alkyl sulfides are observed at neutral pH, and the stability constant of 540 dm^3 mol^{-1} has been reported for diisopropyl sulfide, which also decays by a deprotonation mechanism.[32] A much lower value for the stability constant of dimer radical cations of 1-bromo-*n*-chloroethanes explains the lack of stabilization and their observation only at high acid concentrations. The intercept (Figure 8) is observed to increase with a decrease in HClO$_4$ concentration. At low acid concentrations, the OH adduct may decay by reaction 2 whereas at higher acid concentrations, the OH adduct would form solute radical cations (reaction 3). It is also possible that the neutral radical formed via reaction 5 may react with H$^+$ to produce back the solute radical cation. The intercept is represented by a complex function, which makes it difficult to determine the deprotonation rate constant.

Effect of Solute Structure. The OH radical induced acid-catalyzed oxidation of alkyl iodides was observed at pH = 3.0, and with alkyl bromides, the OH radical induced oxidation was observed at [HClO$_4$] > 2.0 mol dm^{-3}. In the case of 1-bromo-*n*-chloroalkanes, it was observed only when [HClO$_4$] was >5.0 mol dm^{-3}. This shows that the higher acid concentration required for 1-bromo-*n*-chloroalkanes as compared to bromoalkanes is due to the presence of chlorine. The concentration of acid required was also observed to depend on the chain length between bromine and chlorine. A high [H$^+$] is required if the chain length between bromine and chlorine is small. Chlorine, a high electron affinity group, may reduce the electron density at bromine, and therefore a high acid concentration would be required for OH radical induced oxidation of 1-bromo-*n*-chloroalkanes. Chlorine would reduce the electron density at bromine to a great extent if chlorine is very close to bromine, as is the case with bromochloromethane (Figure 2). The amount of acid required is reduced when the chain length between bromine and chlorine is increased. Fluorine was also observed to reduce the electron density at iodine in fluorinated alkyl iodides, and a high concentration of acid was required for OH

radical induced oxidation of fluorinated alkyl iodides as compared to alkyl iodides.[18]

Quantum Chemical Calculations. Theoretical calculations were made to estimate the net atomic charge at bromine in alkyl bromides, 1,*m*-dibromoalkanes, and 1-bromo-*n*-chloroalkanes in their fully optimized geometries at the AM1 level. For comparison purposes, the net atomic charge at the heteroatom was also computed for the case of alkyl chlorides and alkyl iodides (Table 2). It is clear from this table that (i) the net atomic charge at bromine is more positive if the alkyl bromide contains an additional bromine or chlorine atom; (ii) the net atomic charge at the heteroatom becomes more negative with an increase in the methylene linkage, reaching the saturation value with $n \geq 3$; (iii) the ionization potential (IP) values of alkyl halides decrease with an increase in the length of the methylene linkage; and (iv) the IP values decrease if the alkyl halide has a heteroatom with a lower electron affinity value. The longer methylene linkage, which is electron releasing in nature, has decreased the IP value as expected. The variation of charge with $n \geq 3$ is small because the halogen is far off and may not be affected significantly by the increase in the length of the methylene or by the presence of another halogen. The decrease of the negative charge over iodine of an alkyl iodide probably indicates the higher probability for formation of the OH adduct of the alkyl iodide. The low IP values of alkyl iodides compared to those of alkyl chlorides also support this conclusion.

The most stable geometry for the dimer radical cation, [ClCH$_2$Br∴BrCH$_2$Cl]$^+$, was computed after doing a complete search under the UHF/AM1 method. The energy of the above dimeric species at the dissociation limit (r_{Br-Br} is quite large) was also calculated after complete geometry optimization. The difference of the total energy of the dimer radical cation at the most stable geometry and at the dissociation limit was taken as the 2c-3e bond energy of the species. A similar procedure was followed to find out the 2c-3e bond energies in other 1-bromo-*n*-chloroalkanes, and the results are displayed in Table 3. Although the bond energies are different for different systems, the bond distance between two Br atoms is more or less equal
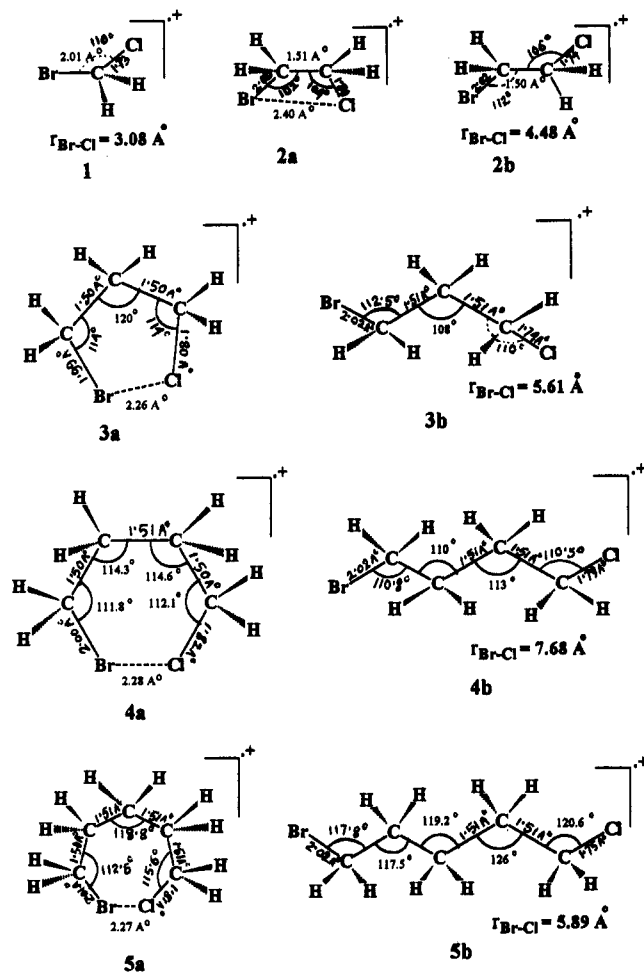
Figure 9. Computed geometrical parameters at the UHF/AM1 level for different radical cations of 1-bromo-*n*-chloroalkanes (*n* = 1−5).

in all the cases. The bond order between a pair of atoms (X and Y) was calculated by following the definition of Mayer.[38] The bond order between two bromine atoms of the dimer radical cations at their most stable geometry is 0.5, and at the dissociation limit it is 0.0 in all the cases. The bond order at their most stable geometry indicates the existence of a 2c-3e bond where two electrons are of bonding σ type and one is of antibonding σ^* character. The spin density and charge are distributed equally over the two Br atoms. Qualitatively, the computed atomic charges over Br atoms increase with 2c-3e bond energies. The $\langle s_z^2 \rangle$ values as seen from Table 3 are 0.75 in all the cases, as expected for a doublet.

The computed geometries of different radical cations of 1-bromo-*n*-chloroalkanes are depicted in Figure 9. The intramolecular 2c-3e bond energy between the oxidized Br atom and the Cl atom in the same molecule was calculated from the difference between the energy of the most stable structure (b) and that of the all trans structure (a), where there is no such bond. The existence of such a bond was characterized by computing the bond order between two heteroatoms. Table 4 displays the computed intramolecular 2c-3e bond energies of radical cations from 1-bromo-*n*-chloroalkanes along with other computed properties. Unlike the case of intermolecular 2c-3e bonding, in the case of intramolecular 2c-3e bonding the radical cation needs a special geometry so that two heteroatoms are close enough to make this bond. It was described earlier that, in the case of bromochloromethane, 1-bromo-3-chloropropane, and 1-bromo-4-chlorobutane, the intramolecular 2c-3e bond could be observed experimentally. The computed results show that although the intramolecular 2c-3e bond is formed in all

TABLE 4: Computed Properties of Two-Center Three-Electron Bond in Intramolecular Radical Cations from 1-Bromo-*n*-chloroalkanes

$\left[\begin{array}{c} Cl \therefore Br \\ (\quad) \\ (CH_2)_n \end{array} \right]^+$	ΔH_f (kcal/mol)	2c-3e bond energy (kcal/mol) (a−b)	bond distance (Br−Cl, Å)	$\langle S_z^2 \rangle$	bond order (Br−Cl)
1 (1)	247.716		3.08	0.75	0.00
2 (2a)	221.051				
(2b)	209.684	11.367	2.42	0.75	0.48
3 (3a)	211.713				
(3b)	178.857	32.856	2.26	0.76	0.50
4 (4a)	220.379				
(4b)	173.870	46.509	2.28	0.76	0.50
5 (5a)	182.352				
(5b)	169.199	13.253	2.27	0.76	0.48

the systems from *n* = 2 to *n* = 5, the bond energies for *n* = 2 and *n* = 5 are very low, which indicates their instability and makes it difficult to detect them in experiments. In the case of the radical cation of bromochloromethane the distance between bromine and chlorine atoms is computed to be 3.08 Å by the AM1 method. Although this quite large distance does not allow the p-orbitals of the two heteroatoms to overlap suitably to make a hemibond, the experimental result shows the formation of the radical cation of bromochloromethane, which must be stabilized on coordination with the p-orbital of the heteroatoms to give the λ_{max} at 380 nm. However, the absorption from intermolecular 2c-3e bonding between two bromine atoms is also present. A solvent-modified quantum chemical calculation at a higher level may give a better understanding at this stage.

As seen from Table 4, in the case of intramolecular bonding also, the bond order between bromine and chlorine atoms is ∼0.5 where there is a hemibond and is ∼0.0 where there is no hemibond. So, one can successfully use quantum chemical bond order as an indicator for the presence of a hemibond instead of localizing the orbitals under the UHF framework, which the present case requires.

Conclusions

The hydroxyl radicals react with 1-bromo-*n*-chloroalkanes and form the respective solute radical cations in the presence of a high H^+ concentration. The high electronegativity of chlorine lowers the electron density at bromine, and thereby a higher H^+ concentration is required for OH radical induced oxidation of 1-bromo-*n*-chloroalkanes as compared to bromoalkanes. There is little variation in the concentration of acid required for OH radical induced oxidation of 1-bromo-*n*-chloroalkanes when *n* ≥ 3 and also little variation in the computed atomic charge over bromine. The dimer radical cation is a strong one-electron oxidant with a redox potential value greater than 2.1. The deprotonation is the rate-determining step for the decay of dimer radical cation. The inter- and intramolecular 2c-3e bond energies of radical cations from 1-bromo-*n*-chloroalkanes are computed at the UHF/AM1 level. The computed bond order has been used as an indicator for the exitence of the 2c-3e bond.

References and Notes

(1) Alfassi, Z. B.; Mosseri, S.; Neta, P. *J. Phys. Chem.* **1989**, *93*, 1380.

(2) Emmi, S. S.; Beggiato, G.; Casalbore-Miceli, G. *Radiat Phys. Chem.* **1989**, *33*, 29.

(3) Sumiyoshi, T.; Sawamura, S.; Koshikawa, Y.; Katayama, M. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 2346.

(4) Vanden Ende, C. A. M.; Luthjens, L. H.; Warmen, J. M.; Hummel, A. *Radiat. Phys. Chem.* **1982**, *19*, 455.

(5) Grodkowski, J.; Neta, P. *J. Phys. Chem.* **1984**, *88*, 1205.

(6) (a) Shoute, L. C. T.; Neta, P. *J. Phys. Chem.* **1990**, *94*, 2447. (b) Shoute, L. C. T.; Neta, P. *J. Phys. Chem.* **1990**, *94*, 7181.

Radical Cations of 1-Bromo-*n*-chloroalkanes

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(7) Mönig, J.; Bahnemann, D.; Asmus, K.-D. *Chem. Biol. Interact.* **1983**, *47*, 15.

(8) Reynolds, E. S.; Moslen, M. T. In *Free Radicals in Biology*; Pryor, W. A., Eds.; Academic Press: New York, 1980; Vol. 4, p 49.

(9) Slater, T. F. In *Free Radical, Lipid Peroxidation and Cancer*; Mcbrien, D. C. H., Slater, T. F., Eds.; Academic Press: London, 1982; p 243.

(10) Recknagel, R. O.; Glende, E. A. Jr.; Hruszkevycz, A. M. In *Free Radicals in Biology*; Pryor, W. A., Ed.; Academic Press: New York, 1977; Vol. 3, p 97.

(11) Kime, Y. J.; Driscolt, D. C.; Dowben, P. A. *J. Chem. Soc., Faraday Trans. 2* **1987**, *83*, 403.

(12) Hamil, W. H. In *Radical Ions*; Kevan, L., Kaiser, E. T., Eds.; Interscience: New York, 1968; 321.

(13) Willard, J. E. In *Fundamental Processes in Radiation Chemistry*; Ausloss, P., Eds.; Interscience Publishers: New York, 1968; p 599.

(14) (a) Mittal, J. P.; Hamill, W. *J. Am. Chem. Soc.* **1967**, *89*, 5749. (b) Andrews, L.; Prochaska, F. T.; Ault, B. S. *J. Am. Chem. Soc.* **1979**, *101*, 9. (c) Simons, J. P.; Tatham, P. E. R. *J. Chem. Soc. A* **1966**, 854. (d) Mohan, H.; Rao, K. N.; Iyer, R. M. *Radiat. Phys. Chem.* **1984**, *23*, 505. (e) Brown, G. P.; Simons, J. P. *Trans. Faraday Soc.* **1969**, *65*, 3245. (f) Bajaj, P. N.; Iyer, R. M. *Radiat. Phys. Chem.* **1980**, *16*, 21.

(15) Mishra, S. P.; Symons, M. C. R. *J. Chem. Soc., Perkin Trans. 2* **1975**, 1492.

(16) (a) Sumioyoshi, T.; Yamada, T.; Ohtaka, A.; Tsugaru, K.; Katayama, M. *Chem. Lett.* **1986**, 307. (b) Sumioyoshi, T.; Yamada; Ohtaka, A.; Tsugaru, K.; Katayama, M. *Hokkaido Daigaku Kogakubu Kenkyu Hokoku* **1988**, *139*, 149.

(17) (a) Mohan, H.; Asmus, K.-D. *J. Chem. Soc., Perkin Trans. 2* **1987**, 1795. (b) Mohan, H.; Asmus, K.-D. *J. Am. Chem. Soc.* **1987**, *109*, 4745. (c) Mohan, H.; Asmus, K.-D. *J. Phys. Chem.* **1988**, *92*, 118.

(18) (a) Mohan, H.; Maity, D. K.; Mittal, J. P. *Chem. Phys. Lett.* **1992**, *194*, 135. (b) Mohan, H.; Maity, D. K.; Mittal, J. P. *J. Chem. Soc., Faraday Trans.* **1993**, *89*, 1477. (c) Mohan, H.; Maity, D. K.; MIttal, J. P. *Chem. Phys. Lett.* **1994**, *220*, 455. (d) Mohan, H.; Mittal, J. P. *J. Chem. Soc., Perkin Trans. 2* **1992**, 1731.

(19) Brühlmann, U.; Büchler, H.; Marchetti, F.; Bühler, R. E. *Chem. Phys. Lett.* **1973**, *21*, 412.

(20) Thomas, J. K. *J. Phys. Chem.* **1967**, *71*, 1919.

(21) Spinks, J. W. T.; Woods, R. J. *Introduction to Radiation Chemistry*; Wiley: New York, 1976; p 247.

(22) (a) Asmus, K.-D. *Acc. Chem. Res.* **1979**, *12*, 436. (b) Asmus, K.-D. In *Sulfur-Centered Reactive Intermediates in Chemistry and Biology*; Chatgilialoglu, C., Asmus, K.-D., Eds.; NATO ASI Series A: Life Sciences: Plenum Press: New York, 1990, Vol. 197, p 155. (c) Hartmut,

H.; Guha, S. N.; Asmus, K.-D. *J. Chem. Soc., Chem. Commun.* **1991**, 999. (d) Anklam, E.; Mohan, H.; Asmus, K.-D. *J. Chem. Soc., Perkin Trans. 2* **1988**, 1297. (e) Bobrowski, K.; Schoneich, C. *J. Chem. Soc., Chem. Commun.* **1993**, 795. (f) Mohan, H.; Mittal, J. P. *J. Chem. Soc., Perkin Trans. 2* **1992**, 207. (g) Petersen, R. L.; Nelson, D. J.; Symons, M. C. R. *J. Chem. Soc., Perkin Trans. 2* **1978**, 225.

(23) Kang, K.; Kim, W. S.; Moon, B. H. *Synthesis* **1985**, 1161.

(24) (a) Priyadarsini, K. I.; Naik, D. B.; Moorthy, P. N.; Mittal, J. P. *Proceedings of the 7th Tihany Symposium on Radiation Chemistry*; Hungarian Chemical Society: Budapest, 1991; p 105. (b) Guha, S. N.; Moorthy, P. N.; Kishore, K.; Naik, D. B.; Rao, K. N. *Proc.—Indian Acad. Sci.* **1987**, *99*, 261.

(25) Fielden, E. M. In *The Study of Fast Processes and Transient Species by Electron Pulse Radiolysis*; Baxendale, J. H., Busi, F., Eds.; D. Reidel: Boston, 1984; p 59.

(26) Vogel, A. I. *A Text Book of Quantitative Inorganic Analysis*; English Language Book Society, Longmans Green and Co.: London, 1961; p 809.

(27) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.

(28) Maity, D. K.; Mohan, H. *Chem. Phys. Lett.* **1994**, *230*, 351.

(29) (a) Neta, P.; Huie, R. E. *J. Phys. Chem. Ref. Data* **1988**, *17*, 1027. (b) Huie, R. E.; Chifton, C. L.; Neta, P. *Radiat. Phys. Chem.* **1991**, *38*, 477.

(30) (a) Elbenberger, H.; Steenken, S.; O'Neill, P.; Schulte-Frohlinde, D. *J. Phys. Chem.* **1978**, *82*, 749. (b) Huie, R. E.; Clifton, C. L. *Int. J. Chem. Kinet.* **1989**, *21*, 611. (c) Clifton, C. L.; Huie, R. E. *Int. J. Chem. Kinet.* **1989**, *21*, 677.

(31) Beilski, B. H. J.; Arudi, R. L.; Sutherland, M. W. *J. Biol. Chem.* **1983**, *258*, 1748.

(32) Choudhri, S. A.; Göbl, M.; Freyholdt, T.; Asmus, K.-D. *J. Am. Chem. Soc.* **1984**, *106*, 5988.

(33) Paul, M. A.; Long, F. A. *Chem. Rev.* **1957**, *57*, 1.

(34) Maity, D. K.; Mohan, H. *J. Chem. Soc., Perkin Trans. 2* **1993**, 2229.

(35) (a) Mohan, H.; Moorthy, P. N. *J. Chem. Soc., Perkin Trans. 2* **1990**, 277. (b) Mohan, H.; Moorthy, P. N. *Radiat. Phys. Chem.* **1989**, *33*, 211.

(36) (a) Bonifačič, M.; Asmus, K.-D. *J. Phys. Chem.* **1976**, *80*, 2426. (b) Asmus, K.-D.; Williams, P. S.; Gilbert, B. C.; Winter, J. N. *J. Chem. Soc., Chem. Commun.* **1987**, 208.

(37) Mönig, J.; Goslich, R.; Asmus, K.-D. *Ber. Bunsen-Ges Phys. Chem.* **1986**, *90*, 115.

(38) Mayer, I. *Chem. Phys. Lett.* **1983**, *97*, 270.