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Hydroxyl radical induced reactions in aqueous solutions of halogenated benzenes: effect of electronegativity of halogen

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Abstract

The ·OH radicals, generated by radiolysis, are found to react only in acidic conditions with halogenated benzenes by an electron transfer mechanism. The concentration of acid, at which solute radical cation of halogenated benzenes appear, is observed to depend strongly on the nature and number of halogen atoms in halogenated benzenes. A linear increase in the acid concentration required for solute radical cation formation is observed with electronegativity of halogen.

1. Introduction

The identity and the reactivity of transient species generated on radiolysis and photolysis of halogenated organic compounds is important as they are frequently employed as pesticides and as solvents for radiation and electrochemical studies [1,2]. In neutral aqueous solutions, the reaction of ·OH radical with alkyl halides depends on the nature of halogen [3–7]. On the other hand, the reaction of ·OH radical with aromatic compounds is known to be by addition to benzene ring forming cyclohexadienyl radical [8–12]. However the fact that ·OH radical is a strong oxidizing species, the electron transfer is observed only in acidic solutions. The halogen centered radical cation of alkyl halides is stabilized on coordination with the free p electron pair of another halogen atom, both by inter- and intra-molecular interation forming a three electron (2s–1s*) bond [6,7]. In the case of aromatic halogenated compounds, the formation of solute radical cation is expected to be a favorable process due to the delocalization of positive charge in the benzene ring [13,14]. In this Letter, we are able to show that halogenated benzenes can form solute radical cation but only in acidic solutions and this is due to high electro negativity of halogen. The concentration of acid required to form solute radical cation of halogenated benzenes is observed to increase with electronegativity of halogen. The presence of five

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fluorine atoms in pentafluoro halogenated benzenes, having high electronegativity, render the ·OH radical-induced electron-transfer reaction a still more difficult process. It is important to know the conditions under which these radical cationic species are formed as this information is essential to determine the their reactivity.

2. Experimental

Halogenated benzenes (C_6H_5X; X = F, Cl, Br, I) and pentafluoro halogenated benzenes (C_6F_5X; X = F, Cl, Br, I) were obtained from Aldrich Chemicals. These halides were washed with aqueous solution of sodium sulfite to remove the last traces of free halogen and then washed with distilled water. The solutions were prepared in 'nanopure' water and freshly prepared solutions were used for each experiment. All other chemicals used were of high purity and used without any further purification.

Pulse radiolysis experiments were carried out with high energy electron pulses (7 MeV, 50 ns) obtained from a linear electron accelerator whose details are available elsewhere [15,16]. The dose per pulse, as determined by $(SCN)_2^{\cdot -}$ dosimeter, was in the range of 10–12 Gy ($1\ \mathrm{Gy} = 1\ \mathrm{J\ kg^{-1}}$). Radiolysis of N_2-saturated neutral aqueous solution ($H_2O \rightarrow {}^{\cdot}OH, {}^{\cdot}H, e_{aq}^-, H_2, H_2O_2, H_3O^+$) leads to the formation of three highly reactive species (${}^{\cdot}OH$, ${}^{\cdot}H$, e_{aq}^-) in addition to the formation of less reactive or inert molecular products (H_2, H_2O_2). The reaction of ·OH radical in neutral solution was carried out in N_2O-saturated conditions, where e_{aq}^- is quantitatively converted to ·OH radicals ($e_{aq}^- + N_2O \rightarrow {}^{\cdot}OH + OH^- + N_2$) with $G(OH) = 5.7$ (G denotes the number of species per 100 eV of absorbed energy ($G = 1$ corresponds to 0.1036 $\mu\mathrm{mol\ J^{-1}}$). The reaction in acidic solutions was carried out in aerated conditions to scavenge $e_{aq}^-(e_{aq}^- + H^+ \rightarrow {}^{\cdot}H + H_2O)$ and ·H atoms (${}^{\cdot}H + O_2 \rightarrow HO_2^{\cdot}$).

The transient species formed on pulse radiolysis were detected by optical absorption method using a 450 W pulsed xenon arc lamp and Kratos monochromator. The photomultiplier output was digitized with a 100 MHz storage oscilloscope interfaced to a computer for kinetic analysis [17]. The rate constant for the reaction of ·OH radicals with halogenated benzenes was determined by formation kinetic studies on monitoring the growth of the transient absorption band, at its λ_{max}, as a function of solute concentration. The pseudo-first-order rate (k_{obs}) increased with solute concentration. The bimolecular rate constant values (k_f) were determined from the linear regression plots of k_{obs} vs solute concentration and the variation was within 10 %. The molar extinction coefficient value (ε_{max}) was determined from the absorbance value at λ_{max} by taking the concentration of the transient species equal to that of ·OH radicals concentration produced on pulse radiolysis under same dose conditions. The absorption-time signal at λ_{max} was analyzed for first and second-order decay kinetics and very good correlation was observed for first-order decay (k_d) between the experimental and calculated results and these values are reported here [17]. The second-order rate constants for the decay of transient bands formed in neutral aqueous solution of C_6F_5X are represented with $2k$ values.

3. Results and discussion

3.1. Reaction of ·OH radical with halogenated benzenes

Pulse radiolysis of N_2O-saturated neutral aqueous solution of halogenated benzenes (C_6H_5X; X = F, Cl, Br, I) has shown the formation of a transient absorption band with λ_{max} in 310–330 nm region (Table 1, Fig. 1a). In the presence of *t*-butyl alcohol (0.3 mol $\mathrm{dm^{-3}}$), an efficient ·OH radical and weak H· atom scavenger, very little transient absorption was seen in 280–400 nm region suggesting that the transient absorption spectra (Fig. 1a) is mainly due to the reaction of ·OH radical with negligible contribution from H· atom reaction. The addition of ·OH radical at the ipso position would result in the formation of phenoxyl radical and halide ion. The phenoxyl radicals have absorption in 360–430 nm [18]. The absence of transient absorption band in this wavelength region, suggest that ·OH radical

Table 1
Kinetic and spectroscopic parameters of the transient species formed on reaction of ·OH radicals with halogenated benzenes (C_6H_5X; X = F, Cl, Br, I) at pH = 7

Reaction	λ_{max} (nm)	σ_{cal}	k_f (10^9 dm^3 mol^{-1} s^{-1})	k_d (10^9 dm^3 mol^{-1} s^{-1})	Probable site of ·OH radical attack	ε_{max} (10^3 dm^3 mol^{-1} s^{-1})
C_6H_5F + ·OH	310	−0.07	5.7	1.1	4	3.2
C_6H_5Cl + ·OH	330	0.11	3.2	1.0	4	6.2
C_6H_5Br + ·OH	325	0.15	5.2	2.2	4	4.4
C_6H_5I + ·OH	325	0.14	2.7	3.4	4	4.5

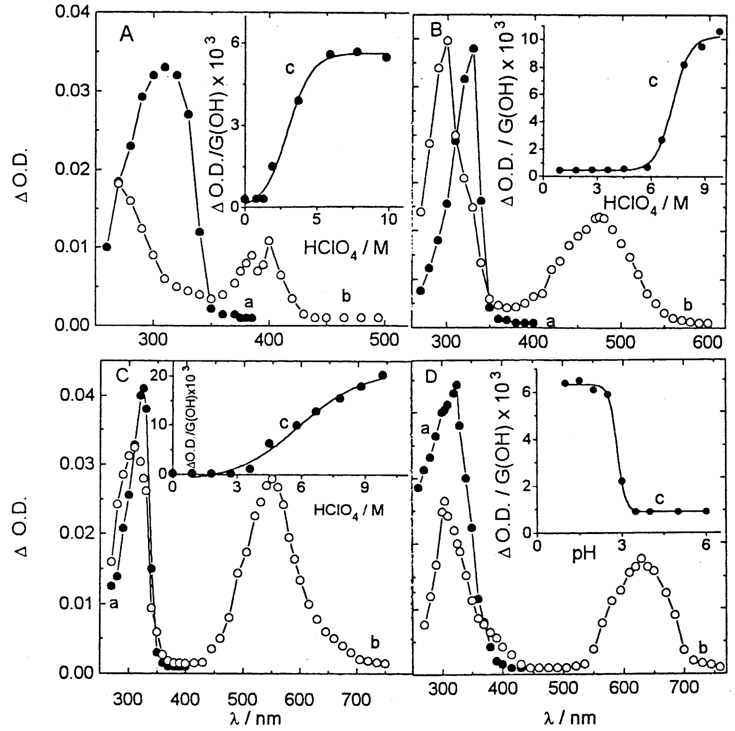
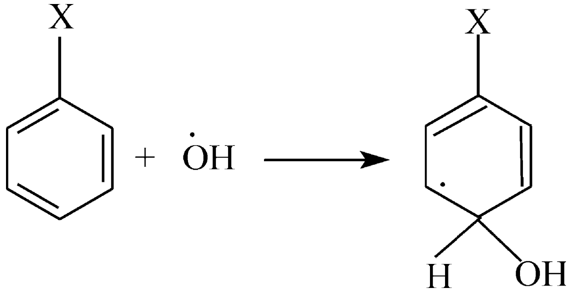


Fig. 1. Transient absorption spectra obtained on pulse radiolysis of halobenzenes [(C_6H_5X; X = F – (A); Cl – (B); Br – (C) I – (D)] of N_2O-saturated neutral aqueous solution – (a) and aerated acidic solutions – (b). Inset shows variation of normalized absorbance as a function of $HClO_4$ concentration – (c).

addition is not taking place at ipso position or the fraction of ·OH radical addition at ipso position is small. The site of ·OH radical attack can be determined if the stable product distribution is known. However, in the absence of such results, the rough idea about probable site of ·OH radical addition could be assessed from Hammett equation by knowing the algebraic sum of the Hammett constants at each position. Taft's constant (σ^*) is taken for *ortho* substitution and σ_p^+ and σ_m^+ are taken for *para* and *meta* substitution, respectively [19,20]. The σ value (σ_{cal}) is calculated for each position and the site with minimum value is expected to be the probable site for ·OH radical addition and is determined to be the *para* position (Table 1). These results support the absence of transient absorption band due to phenoxyl radical. Therefore the reaction of ·OH radicals, in neutral aqueous solution of halogenated benzenes, could be represented by Scheme 1. The transient



Scheme 1.

absorption band of cyclohexadienyl radical, formed on addition of ·OH radical to benzene ring, is observed to decay by second-order kinetics. The spectral and kinetic parameters of the transient species formed on reaction of ·OH radicals with halogenated benzenes are shown in Table 1.

In acidic solutions, the nature of the transient absorption spectrum was entirely different. Fig. 1b shows the transient absorption spectra obtained on pulse radiolysis of aerated acidic aqueous solution of halogenated benzenes. The absorbance of the transient absorption band with λ_{max} at 400, 475, 550 and 630 nm, formed in the case of F, Cl, Br and I benzenes, respectively, increased with $HClO_4$ concentration (inset of Fig. 1). The saturation value of absorbance was observed for C_6H_5I ($HClO_4 = 0.01$ mol dm^{-3}) and C_6H_5F ($HClO_4 = 5.9$ mol dm^{-3}). For C_6H_5Br and C_6H_5Cl, the saturation value of absorbance could not be seen even at the highest available concentration of $HClO_4$. The transient absorption bands at 475 and 550 nm for Cl and Br benzenes, respectively, appear at much higher concentration of $HClO_4$ than for F benzene. Therefore it is expected that the saturation value of absorbance for Cl and Br benzenes would be attained at $HClO_4$ concentration much higher than that of F benzene. The concentration of $HClO_4$ at which the transient absorption band at 400, 475, 550 and 630 nm, are observed, was found to depend strongly on the nature of halogen (Table 2).

The transient absorption bands at 400, 475, 550 and 630 nm observed in acidic solutions could be either due to the reaction of OH-adduct, formed in neutral solution, with H^+ or by an overall reaction involving ·OH radical and H^+ together. If it is formed by the former mechanism, then the decay rate of OH-adduct would depend on H^+ concentration and match with the formation rate of above mentioned bands in acidic solutions. In the latter case, the decay and formation rate constants would be independent of H^+ concentration and only the absorbance value would increase with H^+ concentration. In the present experiments, the decay of OH-adduct and formation rate constants of transient bands in acidic solutions was not affected by H^+ and only the absorbance value increased with H^+ concentration. The Transient absorption bands formed at 400, 475, 550 and 630 nm for F, Cl, Br and I substituted benzenes, respectively should be due to solute radical cation formed on acid-catalyzed dehydration of OH-adduct as represented in Scheme 2. It is reported that for an electron transfer reaction, H_2O is a better leaving group than OH^- [9].

The high electronegativity of halogens would keep the electrons to themselves strongly. The strength with which the electrons are held with the

Table 2

Kinetic and spectroscopic parameters of the transient species formed on reaction of ·OH radicals with halogenated benzenes (C_6H_5X; X = F, Cl, Br, I) in acidic solutions

Reaction	$[HClO_4]$ (mol dm^{-3})	λ_{max} (nm)	k_f (10^9 dm^3 mol^{-1} s^{-1})	k_d (s^{-1})	ε (dm^3 mol^{-1} cm^{-1})	$[HClO_4]$ required to form SRC
C_6H_5F + ·OH	5.9	385, 400	6.1	2.8×10^3	3.6×10^{3a}	1.9
C_6H_5Cl + ·OH	7.8	295, 475	1.7	1.8×10^4	–	6.2
C_6H_5Br + ·OH	7.8	310, 550	8.9	1.4×10^4	–	3.1
C_6H_5I + ·OH	0.1	305, 630	4.7	2.3×10^5	5.4×10^{3b}	0.01

SRC – solute radical cation.

[a] At 400 nm.

[b] At 630 nm

molecule is compensated with the additional energy supplied in the form of H^+ concentration. The concentration of acid required to observe the formation of solute radical cation increased with the electronegativity of halogen (Fig. 2). As the concentration of acid is increased, the equilibrium would shifts towards right direction and absorbance value of solute radical cation is increased. The formation of solute radical cation in acidic solution is due to the fact that the electron withdrawing power of $^{\bullet}OH$ radical is strongly increased in acidic solutions [9]. The concentration of $HClO_4$ required to form the solute radical cation increased with electronegativity of halogen and the nature of transient absorption spectra for these halogenated benzenes was significantly different in each case. Therefore the site of $^{\bullet}OH$ radical attack is expected to at the halogen. Subsequently the equilibrium (Scheme 2) may take over and the charge may stabilize on benzene ring. Depend on the electron withdrawing power (electronegativity) of halogen, different concentrations of acid would be required to shift the equilibrium towards solute radical cation formation. The formation could be observed only when sufficient H^+ concentration is present to compensate for the electron withdrawing power of halogen.

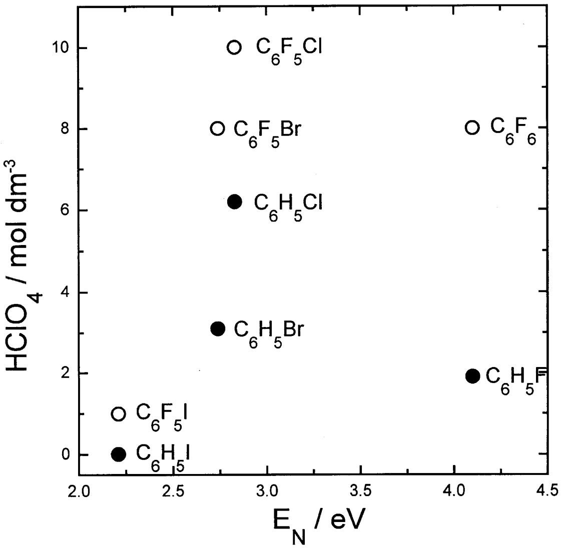
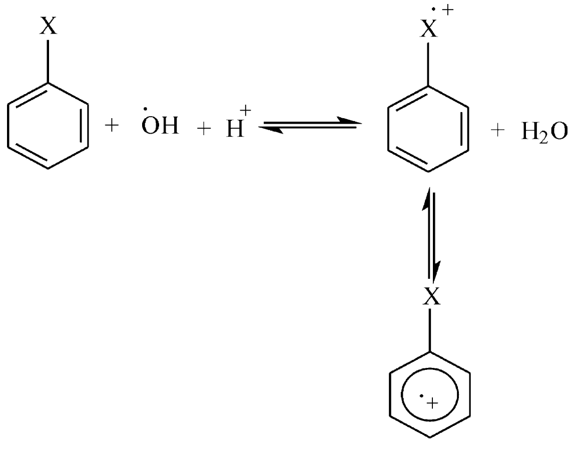


Fig. 2. Variation of $HClO_4$ concentration required for the formation of solute radical cations as a function of electro negativity.



Scheme 2.

In highly acidic solutions, in addition to $^{\bullet}OH$ radicals, other transient species formed may also contribute towards solute radical cation formation and following methods assessed their contributions. The nature of the transient absorption spectra remained same in aerated and N_2-saturated conditions, indicating that the contribution of $H^{\bullet}$ atom reaction with halogenated benzenes is negligible, as $H^{\bullet}$ atoms would be converted to $HO_2^{\bullet}$ radicals, which are weakly oxidizing in nature, and were observed to be uncreative towards halogenated benzenes. (2) In the presence of *t*-butyl alcohol (0.3 mol dm^{-3}) the transient absorption was completely scavenged, showing that the transient absorption spectra is mainly due to the reaction of $^{\bullet}OH$ radicals with halogenated benzenes. (3) The transient species produced from $HClO_4$ radiolysis were not contributing for the formation of solute radical cations of halogenated benzenes as the nature of the transient absorption spectra obtained on reaction of $^{\bullet}OH$ radicals with halogenated benzenes remained same in H_2SO_4 also.

3.2. Reaction of $^{\bullet}OH$ radical with pentafluoro halogenated benzenes

Pulse radiolysis of N_2O-saturated neutral aqueous solution of pentafluoro halogenated benzenes (C_6F_5X; X = F, Cl, Br, I) have shown the formation of two transient absorption bands. The

Table 3
Kinetic and spectroscopic parameters of the transient species formed on reaction of ·OH radicals with pentafluoro halogenated benzenes (C_6F_5X; X = F, Cl, Br, I) at pH = 7

Reaction	λ_{max} (nm)	k_f ($dm^3\ mol^{-1}\ s^{-1}$)	$2k$ ($dm^3\ mol^{-1}\ s^{-1}$)	ε_{max} ($dm^3\ mol^{-1}\ s^{-1}$)
$C_6F_5F + {}^{\bullet}OH$	<270, 395	1.6×10^9	6.2×10^8	1×10^3 (395 nm)
$C_6F_5Cl + {}^{\bullet}OH$	285, 400	4.9×10^8	8.6×10^8	3.5×10^3 (285 nm)
$C_6F_5Br + {}^{\bullet}OH$	290, 405	4.5×10^8	7.8×10^8	2.7×10^3 (290 nm)
$C_6F_5I + {}^{\bullet}OH$	290, 400	1.2×10^9	5.2×10^9	3×10^3 (290 nm)

λ_{max} of first band was in 285–290 nm region except for C_6F_6 whose λ_{max} could not be determined and it may be < 270 nm. (Table 3, Fig. 3a). The λ_{max} of second band was in 395–405 nm region (Table 3, Fig. 3a). The addition of ·OH radical at any position would result in the formation of phenoxyl radical with halide ion elimination (Scheme 3) [18].

The entire spectrum decayed by second-order kinetics (Table 3), which was not affected in aerated solutions, indicating that the transient absorption bands are not due to a carbon-centered radical. The transient absorption at 290 nm, formed on reaction of ·OH radical with C_6F_5Br, was completely quenched in presence of low concentration of C_2H_5SH (0.5×10^{-4} mol dm^{-3}). It should be due to abstraction of H· atom from thioethanol (Reaction (1)).

$$C_6F_5O^{\bullet}/C_6F_4BrO^{\bullet} + C_2H_5SH \rightarrow C_6F_5OH/C_6F_4BrOH + C_2H_5S^{\bullet} \quad (1)$$

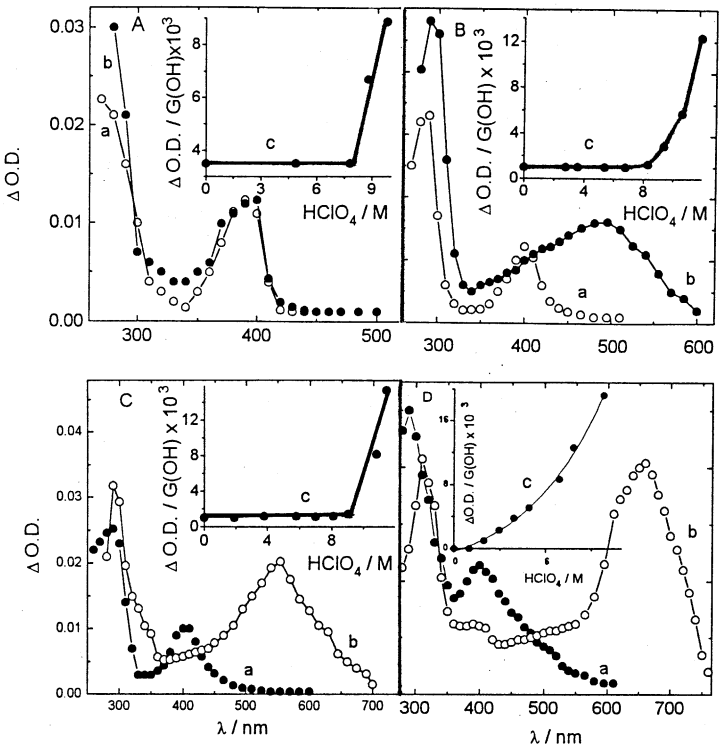
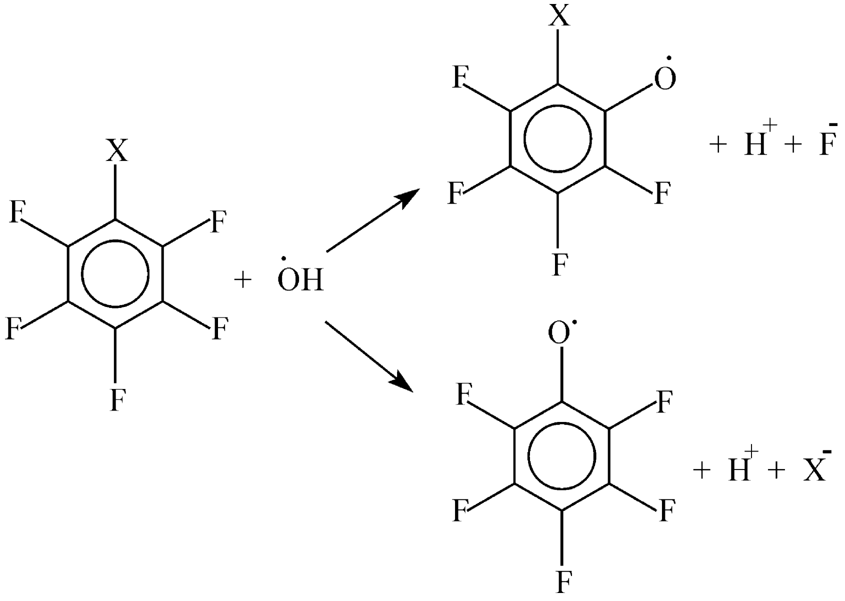


Fig. 3. Transient absorption spectra obtained on pulse radiolysis of pentafluoro halobenzenes [(C_6F_5X; X = F – (A); Cl – (B); Br – (C) I – (D)] of N_2O-saturated neutral aqueous solution – (a) and aerated acidic solutions – (b). Inset shows variation of normalized absorbance as a function of $HClO_4$ concentration – (c).



Scheme 3.

The nature of the transient absorption spectra remained same in pH 1–10 region, however in highly acidic solutions, the nature of spectra was different and was observed to depend on the nature of halogen (Fig. 3b). The kinetic and spectroscopic parameters of the transient species formed on reaction of $^{\bullet}OH$ radicals in aerated acidic solutions of pentafluoro halogenated benzenes (C_6F_5X; X = F, Cl, Br, I) are shown in Table 4. The absorbance of the transient absorption bands at 400, 480, 550 and 660 nm for F, Cl, Br and I substituted pentafluoro benzenes, respectively, increased with $HClO_4$ concentration and the saturation value could not observed in any case (inset of Fig. 3). Except for C_6F_5I, the concentration of acid at which these transient absorption bands appear, is very high (>8 mol dm^{-3}). In comparison to C_6H_5X, very high concentration of $HClO_4$ was required to observe the formation of transient absorption bands of C_6F_5X (Tables 3 and 4, Fig. 2). This should be due to the presence of highly electronegative five fluorine atoms in each case. The concentration of $HClO_4$, required for the formation of these transient absorption bands increased with electronegativity of halogen (Fig. 2). Considering all these results, the formation of solute radical cation of pentafluoro halogenated benzenes require very high concentration of $HClO_4$ and could also be represented in a manner similar to that shown in Scheme 6. Initially the charge is located on halogen (X) and then it is delocalized on benzene ring. The nature of the transient absorption spectra obtained

Table 4

Kinetic and spectroscopic parameters of the transient species formed on reaction of $^{\bullet}OH$ radicals with pentafluoro halogenated benzenes (C_6F_5X; X = F, Cl, Br, I) in acidic solutions

Reaction	$[HClO_4]$ (mol dm^{-3})	λ_{max} (nm)	k_f (10^9 dm^3 mol^{-1} s^{-1})	k_d (s^{-1})	$[HClO_4]$ required to form SRC
$C_6F_5F + {}^{\bullet}OH$	9.8	<280, 400	2.1×10^9	1.6×10^3	8
$C_6F_5Cl + {}^{\bullet}OH$	11.9	290, 480	1.5×10^9	9.9×10^4	10
$C_6F_5Br + {}^{\bullet}OH$	11.7	290, 550	1.5×10^9	8.8×10^4	8
$C_6F_5I + {}^{\bullet}OH$	6.9	310, 660	5.5×10^9	5.2×10^4	1

SRC – solute radical cation.

on reaction of $^{\cdot}$OH radicals in acidic solutions with C_6F_5X was similar to those obtained with C_6H_5X. Therefore, the site of attack could be similar.

3.3. Evidences in support to the formation of solute radical cation

(1) The unambiguous assignment of transient absorption bands, formed on reaction of $^{\cdot}$OH radical with the solute in acidic conditions, to solute radical cation could be made if similar transient absorption spectrum is also obtained on reaction with specific one-electron oxidant. The transient decay of $Cl_2^{\cdot -}$ was observed to become faster in the presence of low concentration of C_6H_5I (inset of Fig. 4) and was observed to react with a bimolecular rate constant of 3.5×10^8 $dm^3 mol^{-1} s^{-1}$. Time resolved studies showed the formation of transient absorption bands at 305 and 630 nm (Fig. 4a), similar to those formed on reaction with $^{\cdot}$OH radicals with C_6H_5I in acidic solution and thus confirm the assignment of transient absorption bands to $C_6H_5I^{\cdot +}$. The transient decay of $Br_2^{\cdot -}$ was not affected on addition of low concentration of C_6H_5 I, suggesting the absence electron transfer reaction. These studies suggest that the oxidation potential of $C_6H_5I/C_6H_5I^{\cdot +}$ couple is between 1.6 and 2.1 V and therefore $C_6H_5I^{\cdot +}$ should be able to undergo electron transfer reaction with anions of lower oxidation potential. It was observed to react with I^- with a rate constant of 8.2×10^9 $dm^3 mol^{-1} s^{-1}$ (Table 5) and showed the formation of a transient band at 385 nm, which is due to $I_2^{\cdot -}$. These studies confirm that the transient bands produced on reaction of $^{\cdot}$OH radical with C_6H_5I are due to solute radical cation. $Cl_2^{\cdot -}$ was not able to undergo electron transfer reaction with C_6H_5Cl and C_6H_5F. The transient absorption band ($\lambda = 460$ nm) of $SO_4^{\cdot -}$, formed on pulse radiolysis of N_2-saturated aqueous solution of $S_2O_8^{2-}$ (4×10^{-2} mol dm^{-3}, *t*-butyl alcohol = 0.3 mol dm^{-3}) was observed to decay faster in presence of low concentration of C_6F_5Br and the bimolecular rate constant was determined to be $\leqslant 1 \times 10^8$ dm^3 mol^{-1} s^{-1}. However, time-resolved studies have not shown the formation of absorption band at 550 nm, suggesting that the solute radical cation is not stable under neutral conditions. The reaction of $^{\cdot}$OH radical with C_6F_5Br has also failed to generate solute radical cation under neutral conditions.

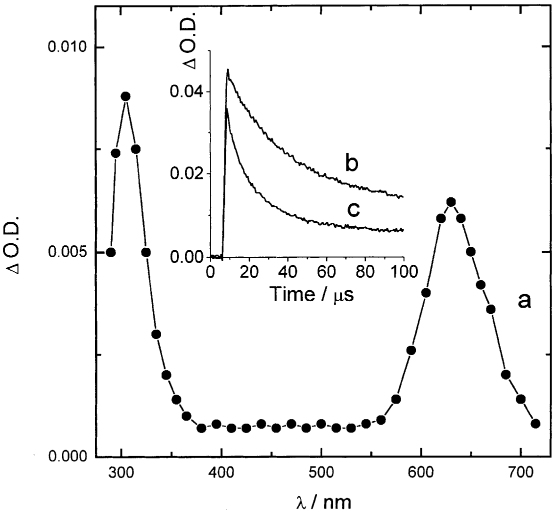


Fig. 4. Transient absorption spectrum obtained on pulse radiolysis of aerated aqueous solution of Cl^- (6×10^{-1} mol dm^{-3}, pH = 1) containing C_6H_5I (0.6×10^{-3} mol dm^{-3}) immediately after the pulse in 450–710 nm and 80 μs after the pulse in 285–385 nm region – (a). Absorption-time profiles of $Cl_2^{\cdot -}$ at 345 nm in absence – (b) and presence of C_6H_5I – (c).

(2) 1,2-Dichloroethane (DCE) has been employed as a solvent for the study of solute radical cation due to its high ionization potential (11.1 eV) [21]. The yield of solvent cations is increased because the electrons produced by ionizing radiation (reaction (2)) are scavenged by the parent molecule and undergo dissociative electron capture (reaction (3)).

$$CH_2ClCH_2Cl \rightarrow (CH_2ClCH_2Cl)^{\cdot +} + e^- \qquad (2)$$

$$CH_2ClCH_2Cl + e^- \rightarrow CH_2Cl^{\cdot}CH_2 + Cl^- \qquad (3)$$

Table 5
Bimolecular rate constant values for the reaction of solute radical cations of halogenated benzenes with inorganic ions

Reaction	Bimolecular rate value (dm^3 mol^{-1} s^{-1})
$(C_6H_5I)^{\cdot +} + I^-$	8.2×10^9
$(C_6H_5I)^{\cdot +} + Br^-$	1.5×10^9
$(C_6H_5Br)^{\cdot +} + Br^-$	7.0×10^9
$(C_6F_5I)^{\cdot +} + Br^-$	3.2×10^9
$(C_6F_5I)^{\cdot +} + Cl^-$	1.7×10^9

The ionization potential of halogenated benzenes is in the range 8–10 eV and is lower than that of DCE. Therefore, it should be possible for solvent cations to transfer their charge to solute molecules (reaction (4)).

$$(\mathrm{CH_2ClCH_2Cl})^{\cdot+} + \mathrm{C_6H_5X/C_6F_5X} \rightarrow \mathrm{CH_2ClCH_2Cl} + (\mathrm{C_6H_5X/C_6F_5X})^{\cdot+} \quad (4)$$

Pulse radiolysis of a N_2-saturated solution of C_6H_5Br in DCE showed the formation of transient absorption band at 570 nm with increasing absorption at $\lambda < 300$ nm. The transient absorption band in the visible region matched with that obtained on pulse radiolysis of acidic aqueous solution of C_6H_5Br and thus support its assignment to solute radical cation. The transient absorption bands obtained on pulse radiolysis of N_2-saturated solution of other halogenated benzenes in DCE also matched with those formed in acidic aqueous solutions.

4. Conclusions

In halogenated benzenes (C_6H_5X, C_6F_5X), $^{\cdot}OH$ radicals are able to undergo electron transfer reaction only in acidic solutions and concentration of acid required for acid-catalysed dehydration depends on the nature of halogen. Due to high electronegativity of halogen, the electrons are held with the molecules very strongly and very high energy is required to remove the electrons. The energy required for the formation of solute radical cation is supplied in the form of H^+ as H_2O is easier to remove as compared to OH^-. Equilibrium exists for the formation of solute radical cation, which is favored in acidic solutions. The concentration of acid required observing the formation of solute radical cation of halogenated benzenes increases with electronegativity of halogen. The presence of five highly electronegative fluorine atoms in C_6F_5X make $^{\cdot}OH$ radical induced electron transfer a difficult process.

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