Pulse Radiolysis Investigations on Acidic Aqueous Solutions of Benzene: Formation of Radical Cations[†]

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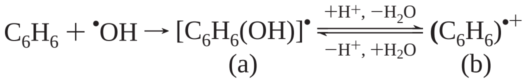
The transient optical absorption bands ($\lambda_{max} = 310$, 350−500 nm, $k = 5.6 \times 10^9$ dm^3 mol^{-1} s^{-1}) formed on pulse radiolysis of an acidic ($HClO_4 = 7.8$ mol dm^{-3}) aqueous solution of benzene are assigned to the solute radical cation formed on acid-catalyzed dehydration of the OH adduct. The solute radical cation is able to undergo an electron transfer reaction with Br^- with a bimolecular rate constant of 8×10^9 dm^3 mol^{-1} s^{-1}. On the other hand, the OH adduct ($\lambda_{max} = 310$ nm) was oxidized by $Fe(CN)_6^{3-}$ with a bimolecular rate constant of 6.6×10^7 dm^3 mol^{-1} s^{-1}. The radical cation of benzene is a strong one-electron oxidant with oxidation potential in the range 2.1−2.4 V vs NHE.

1. Introduction

The knowledge of the photophysical properties of benzene and its molecular ions are important to understand the intrinsic nature of its aromaticity. The recent advances in the methods of generation and detection of transient intermediates have made the radical ion chemistry an active area of research in both the gas and condensed phases.[1] In the past, the nature of the transient intermediates formed on γ-radiolysis and photolysis of organic compounds in the condensed phase was studied from the effect of the known hole and electron scavengers on the optical absorption bands and electron spin resonance measurements.[2−4] With the availability of ultrafast techniques, the time-resolved studies using pulse radiolysis and laser flash photolysis have been employed to obtain independent experimental evidence for the formation of transient intermediates.[5−11] In the aqueous solutions, the reaction of $^{\bullet}OH$ radicals has been the most extensively studied, as they can undergo a variety of reactions (abstraction, addition, electron transfer).[12−15] The hydroxyl radicals react with benzene and substituted derivatives by an addition reaction forming hydroxycyclohexadienyl type radicals.[13−17] The hydroxyl radicals and specific one-electron oxidants are able to undergo electron transfer reaction and form a solute radical cation in the presence of electron-donating substituents such as $-CH_3$ and $-OCH_3$ groups.[18−24] The radical cations of biphenyl and naphthalene have also been inferred as the transient species formed on radiolysis of acidic aqueous solution.[24,25] In spite of the high oxidation potential of the $^{\bullet}OH$ radicals ($E° = 2.73$ V vs NHE at pH = 0), one-electron oxidation of the substituted benzenes containing electron-withdrawing groups (halogens) has not been reported. This is due to the fact that the rate of the reverse reaction (Scheme 1) is very high and the solute radical cations could not be observed. On the basis of the photoionization studies on benzene, the lifetime of the benzene radical cation was estimated to be ∼20 ns.[21] In the presence of electron-donating substituent, ($-CH_3$), the lifetime of the radical cation of toluene is ∼30 ns at pH = 5−6 and increases at lower pH. In the case of methoxy substituents, the stability of the radical cation is high enough and it could be observed even at pH = 6−7.[19,26] Considering the increase in the lifetime of the radical cation at lower pH, we have carried out the pulse radiolysis studies of halogenated benzenes, in highly acidic solutions, and the transient absorption band observed in the visible region was assigned to the solute radical cation.[27] Acid-catalyzed oxidation of a number of organic compounds has also been reported.[28] With the successful stabilization of the solute radical cation of halogenated benzene in highly acidic solutions, now the pulse radiolysis studies on acidic aqueous solutions of benzene have been carried out and the spectral changes observed in acidic solutions are inferred as due to the stabilization of the benzene radical cation. Although the absorption bands of the benzene radical cation formed on γ-radiolysis in a glassy matrix at 77 K,[2,29,30] photoionization studies,[31] and fluorescence spectrum[32] are known, hydroxyl radical induced formation of benzene radical cations is not reported. With this objective, pulse radiolysis studies on acidic aqueous solutions of benzene have been carried out and the formation of the benzene radical cation and its redox properties are discussed in the manuscript.

SCHEME 1



$$\underset{}{C_6H_6} + {}^{\bullet}OH \rightarrow \underset{(a)}{[C_6H_6(OH)]^{\bullet}} \underset{-H^+,\,+H_2O}{\overset{+H^+,\,-H_2O}{\rightleftharpoons}} \underset{(b)}{(C_6H_6)^{\bullet +}} \qquad (1)$$

2. Experimental Section

Spectrograde benzene (purity >99%) was used for pulse radiolysis experiments. Some of the experiments were carried out with HPLC grade (thiophene free) benzene. The solutions were prepared in deionized "nanopure" water and freshly prepared solutions were used for each experiment. $HClO_4$ (60%, analar grade) was used for preparation of acidic solutions. The reaction of $^{\bullet}OH$ radicals in neutral aqueous solutions was carried out in N_2O saturated conditions to convert e_{aq}^- to $^{\bullet}OH$ radicals ($e_{aq}^- + N_2O \rightarrow {}^{\bullet}OH + OH^- + N_2$). Considering the volatile nature of benzene (BP = 80 °C), N_2O saturated water was used for the preparation of solutions, and benzene was introduced through a rubber septum. The reaction of $^{\bullet}OH$ radicals in acidic solutions was carried out in aerated conditions to scavenge e_{aq}^-

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and $^{\bullet}H$ atoms ($H^+ + e_{aq}^- \rightarrow {}^{\bullet}H + H_2O$; ${}^{\bullet}H + O_2 \rightarrow HO_2^{\bullet}$). Under these conditions, there would not be any loss of benzene on account of gas bubbling. The optical absorption studies in the 240−300 nm region showed the presence of benzene in acidic solutions. Pulse radiolysis experiments were carried out with high-energy electron pulses (7 MeV, 50 ns), which were obtained from a linear electron accelerator whose details are reported elsewhere.[33] The dose absorbed by the sample was determined by a KSCN dosimeter,[34] and it was close to 15 Gy per pulse (1 Gy = 1 J kg^{-1}). The photomultiplier output was digitized using a 100 MHz storage oscilloscope interfaced to a computer for kinetic analysis.[35] The pseudo-first-order rate constant (k_{obs}) was determined from the plot of ln (OD) vs time. The bimolecular rate constant values were calculated from the linear plot of k_{obs} vs solute concentration. The rate constant values were the average of three experiments, and the variation was within ±15%.

3. Results and Discussion

Reaction of $^{\bullet}$OH Radicals in Neutral Solutions. The transient optical absorption spectrum obtained on pulse radiolysis of a N_2O-saturated aqueous solution (pH = 6) of benzene (2×10^{-3} mol dm^{-3}) exhibits an absorption band with $\lambda_{max} = 310$ nm, which decayed by second-order kinetics. The bimolecular rate constant for the reaction of $^{\bullet}$OH radicals with benzene, determined by formation kinetic studies at 310 nm (6.5×10^9 dm^3 mol^{-1} s^{-1}) was close to the value determined by competition kinetics (5.1×10^9 dm^3 mol^{-1} s^{-1}) using KSCN as the standard solute. The molar absorptivity of the transient band ($\lambda = 310$ nm), determined by the direct optical absorption method was 3.1×10^3 dm^3 mol^{-1} cm^{-1}, close to the value determined by the competition kinetic method (3.2×10^3 dm^3 mol^{-1} cm^{-1}) using the molar absorptivity of $(SCN^{\bullet})_2^-$ species at 472 nm = 7580 dm^3 mol^{-1} cm^{-1}.[36] These studies suggest that the overall reaction of $^{\bullet}$OH radicals with benzene is by addition to the benzene ring, forming the hydroxycyclohexadienyl radical (a, Scheme 1), and the kinetic parameters are similar to the reported values.[13−17]

Reaction of $^{\bullet}$OH Radicals in Low Acidic Concentrations. It is known that the OH adduct of halogenated organic compounds can undergo acid-catalyzed dehydration to form the solute radical cation.[27] In acidic solutions, the yield of $^{\bullet}$H atoms would increase due to the reaction of H^+ with e_{aq}^-. Therefore, the $^{\bullet}$H atoms should either be scavenged or the contribution of its reaction with benzene should be determined separately. The pulse radiolysis studies in aerated acidic (pH = 1) solutions of benzene showed that (1) the contribution of $^{\bullet}H/HO_2^{\bullet}$ reaction with benzene is small, (2) the reaction of $^{\bullet}$OH radicals in acidic solution can be studied in aerated solutions without any interference from $^{\bullet}H/HO_2^{\bullet}$ radicals, and (3) the acid-catalyzed dehydration of the OH adduct of benzene does not take place at pH = 1.

Reaction of $^{\bullet}$OH Radicals in High Acidic Concentrations. In highly acidic solutions, the entire radiation energy would not be absorbed by water alone, and $G(^{\bullet}OH)$ would decrease with increasing concentration of $HClO_4$ as the radiolysis of $HClO_4$ does not produce $^{\bullet}$OH radicals.[37] On the basis of the electron density variation between water and $HClO_4$, the absorbance values are normalized with respect to $G(^{\bullet}OH)$. The variation of the absorbance at 310 nm, as a function of $HClO_4$ concentration, formed on pulse radiolysis of an aerated acidic aqueous solution of benzene, is shown in Figure 1. The absorbance increased with $HClO_4$ concentration, reaching a saturation value when $HClO_4$ was in the range 7−10 mol dm^{-3}, indicating that the entire yield of $^{\bullet}$OH radicals have reacted with benzene. Under these conditions, the molar absorptivity at 310 nm was determined to be 12.5×10^3 dm^3 mol^{-1} cm^{-1}. The intercept represents the absorbance of OH adduct at 310 nm in neutral solutions.

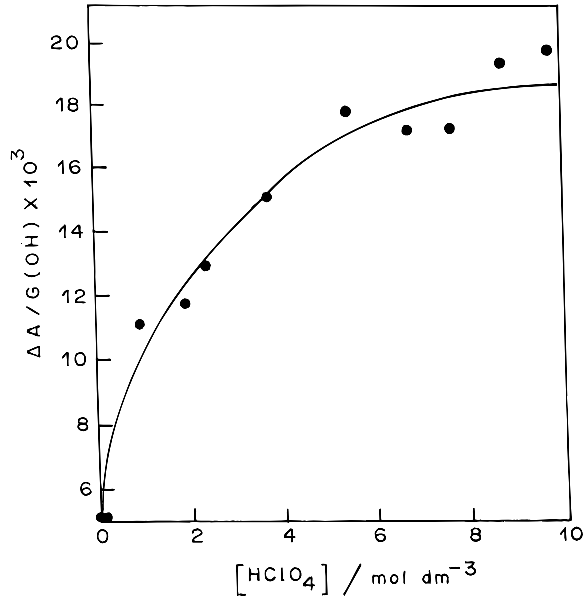

Figure 1. Variation of normalized absorbance at 310 nm formed on pulse radiolysis of aerated aqueous solution of benzene (2×10^{-3} mol dm^{-3}) as a function of $[HClO_4]$.

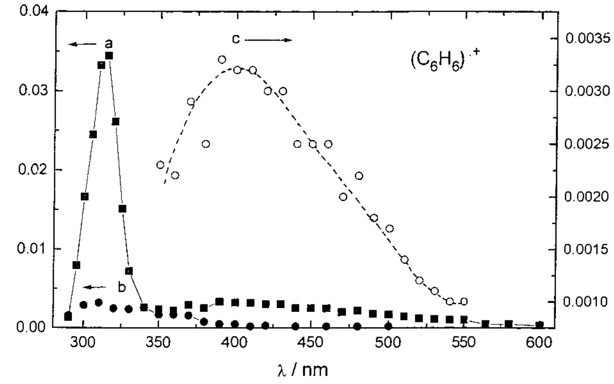

Figure 2. Transient optical absorption spectra obtained on pulse radiolysis of an aerated acidic ($HClO_4$ = 7.8 mol dm^{-3}) aqueous solution in the presence (2×10^{-3} mol dm^{-3}) (a) and absence of benzene (b). The spectrum (a) in 350−550 nm region is shown in expanded scale as (c).

Parts a and b of Figure 2 show the transient optical absorption spectra obtained on pulse radiolysis of an aerated acidic aqueous solution of $HClO_4$ (7.8 mol dm^{-3}) in the presence and absence of benzene, respectively. The bimolecular rate constant for the reaction of $^{\bullet}$OH radicals with benzene in 7.8 mol dm^{-3} $HClO_4$, as determined by formation kinetic studies, was 5.6×10^9 dm^3 mol^{-1} s^{-1}. The band at 310 nm decayed by first-order kinetics with $k = 3.9 \times 10^5$ s^{-1}. In addition to the intense band at 310 nm, a small broad absorption band at 350−500 nm, with a peak at 400 nm, was also observed (shown as (c) in the expanded scale in Figure 2).

Assignment of Transient Absorption Band in Highly Acidic Conditions. The formation of the transient absorption bands (Figure 2a) in highly acidic solutions may be due to the following factors: (1) The 310 nm band in highly acidic solutions (Figure 2a) is not due to the radiolysis product of

$HClO_4$, as the band was not observed in the absence of benzene (Figure 2b). Pulse radiolysis of concentrated acidic solutions of $HClO_4$ had shown the formation of a transient absorption band at $\lambda_{max} = 350$ with a low yield and molar absorptivity and which was assigned to ClO_3 radicals.[37] $HClO_4^{\bullet+}$ with $\lambda_{max} = 440$ nm is formed only when the concentration of $HClO_4$ was more than 10 mol dm^{-3}.[37] (2) The absorption band is also not due to the reaction of transient species produced from radiolysis of $HClO_4$ with benzene, as a similar band was also observed in H_2SO_4. Pulse radiolysis of an aerated acidic ($H_2SO_4 = 8.5$ mol dm^{-3}) solution of benzene (1×10^{-3} mol dm^{-3}) showed an optical absorption band with $\lambda_{max} = 315$ nm ($k = 3.6 \times 10^9$ dm^3 mol^{-1} s^{-1}) with nearly the same molar absorptivity. (3) The band is also not due to the high ionic strength of $HClO_4$, as it was not produced on pulse radiolysis of neutral aqueous solution of $NaClO_4$ (7.8 mol dm^{-3}) containing benzene (1×10^{-3} mol dm^{-3}). (4) The solute is stable in the matrix, as the ground state optical absorption spectrum did not show any change within the experimental time. Therefore, the transient absorption band is not due to the decomposition of the solute. (5) The band is neither due to $^{\bullet}H/HO_2^{\bullet}$ radicals nor due to their reaction with the solute, as the studies in the presence of *tert*-butanyl alcohol, an efficient $^{\bullet}OH$ and weak $^{\bullet}H$ atom scavenger, have not shown the formation of the transient absorption band at 310 nm and $^{\bullet}H/HO_2^{\bullet}$ radicals have absorption well below 300 nm.[38] (6) The transient bands are also not due to any contribution from thiophene, present as an impurity, as pulse radiolysis studies with thiophene free benzene (HPLC grade) have also produced transient absorption bands similar to those shown in Figure 2a. Moreover, the presence of thiophene as an impurity would have given absorption of its radical cation even in neutral solutions and relatively intense absorption in the visible region.[39] Moreover, the increase in the absorbance at 310 nm as a function of [$HClO_4$] at constant benzene concentration (Figure 1) cannot be due to thiophene present as an impurity in benzene.

From these studies, it is clear that the transient bands are due to the reaction of $^{\bullet}OH$ radicals with benzene in the presence of a high concentration of H^+. The redox studies (see text) also suggest the cationic nature of the transient optical absorption band. Hence, we propose that these bands may be assigned to solute radical cation, formed on the acid-catalyzed dehydration of OH adduct (b, Scheme 1). Under high acidic conditions, the rate of the reverse reaction would decrease. Although the position of transient absorption band (310 nm) in neutral and acidic solutions is the same and the broad absorption in the visible region is very small, its decay kinetics and molar absorptivity were different and suggest that the bands observed in neutral and acidic solutions are due to different species. Additional evidence in support of this has been obtained from the different redox behaviors under two different conditions.

Effect of Solute Concentration. Thc variation of the absorbance and decay kinetics of the transient absorption band ($\lambda = 310$ nm) were studied as a function of solute concentration to investigate any possible contribution of dimer radical cations. Due to solubility limitations, the studies were restricted to $(0.6-3) \times 10^{-3}$ mol dm^{-3} concentration of the solute. In this concentration range, both the absorbance and decay kinetics of the transient absorption band formed on pulse radiolysis of an aerated acidic ($HClO_4 = 7.8$ mol dm^{-3}) aqueous solution of benzene remained independent, suggesting that the band is due to a monomeric species. Photoionization in an argon matrix has shown the formation of a dimer radical cation absorbing in the near infrared region.[31]

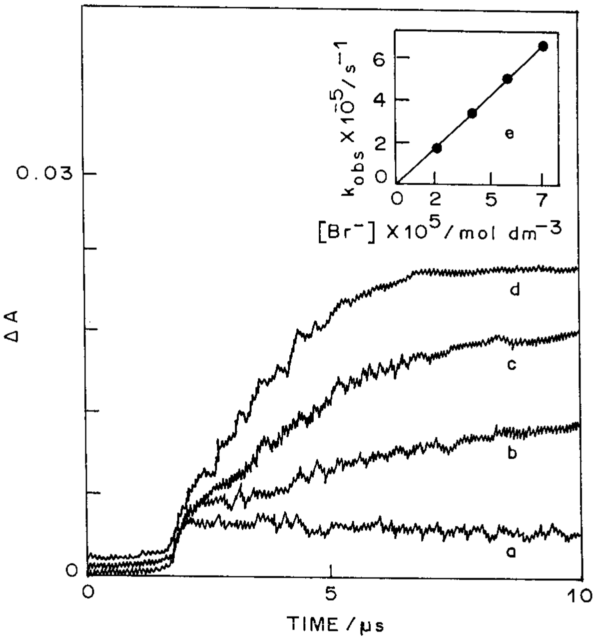

Figure 3. Absorption−time signal (360 nm) formed on pulse radiolysis of an aerated acidic ($HClO_4 = 7.8$ mol dm^{-3}) aqueous solution of benzene (3×10^{-3} mol dm^{-3}) in the presence of different concentrations of Br^-: 0 (a), 1.5 (b), 4 (c), and 6×10^{-5} mol dm^{-3} (d). The inset shows the variation of the first-order rate (k_{obs}) as a function of Br^- concentration (e).

Redox Properties of Benzene Radical Cation. The radical cations are shown to be oxidizing in nature, whereas the OH adduct of benzene and substituted derivatives can be oxidized by oxidants such as $Fe(CN)_6^{3-}$.[13] The transient species formed on pulse radiolysis of an aerated acidic ($HClO_4 = 7.8$ mol dm^{-3}) aqueous solution of benzene (3×10^{-3} mol dm^{-3}) was observed to react with Br^- and formed a transient optical absorption band with $\lambda_{max} = 360$ nm. The bimolecular rate constant, determined from the growth of the 360 nm band for different concentrations of Br^- $(1-6) \times 10^{-5}$ mol dm^{-3} was 8×10^9 dm^3 mol^{-1} s^{-1} (Figure 3). Under these conditions, the $^{\bullet}OH$ radicals would initially react with benzene and the transient species formed would then react with Br^- to form the band at 360 nm (reaction 2). This band is due to $Br_2^{\bullet-}$, and its formation suggest that the redox potential value of $C_6H_6/C_6H_6^{\bullet+}$ couple is more than that of the $Br_2^{\bullet-}/2\ Br^-$ couple (1.63 V vs NHE).

$$(C_6H_6)^{\bullet+} + Br^- \xrightarrow{Br^-} Br_2^{\bullet-} + C_6H_6 \qquad (2)$$

The $SO_4^{\bullet-}$ radical anion is a strong one-electron oxidant with an oxidation potential of 2.43 V vs NHE. It was observed to react with benzene with a bimolecular rate constant of $\sim 1 \times 10^8$ dm^3 mol^{-1} s^{-1} and formed a transient optical absorption band with $\lambda_{max} = 310$ nm. It should be due to the OH adduct of benzene, formed on hydration of the solute radical cation. It is known that the reaction of $SO_4^{\bullet-}$ with substituted benzenes results in the formation of solute radical cation, which undergoes hydration to form the OH adduct.[14] The decay of the transient optical absorption band of $Cl_2^{\bullet-}$, formed on pulse radiolysis of aerated acidic (pH = 1) aqueous solution of Cl^- (2×10^{-2} mol dm^{-3}), was not affected on addition of low concentrations of benzene $(1-7) \times 10^{-5}$ mol dm^{-3}, suggesting the absence of electron transfer from benzene to $Cl_2^{\bullet-}$. These studies suggest that the oxidation potential of the $C_6H_6/C_6H_6^{\bullet+}$ couple is between 2.09 and 2.43 V.

The OH adduct formed in neutral solutions failed to react with Br^- and I^-. On the other hand, it was observed to react

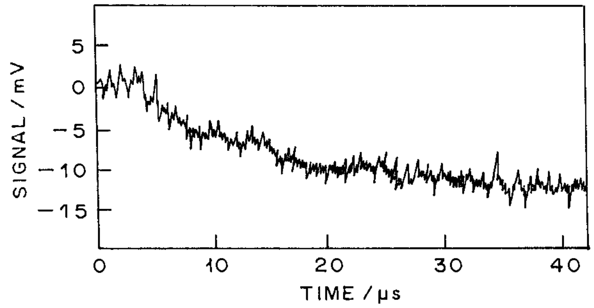

Figure 4. Absorption−time signal (420 nm) obtained on pulse radiolysis of N_2O-saturated neutral aqueous solution of benzene (1×10^{-3} mol dm^{-3}) containing $Fe(CN)_6^{3-}$ (1×10^{-3} mol dm^{-3}).

TABLE 1: Parameters for the Formation of Radical Cations of Halogenated Benzenes (C_6H_5X)

X	[$HClO_4$] required for radical cation/mol dm^{-3}	electronegativity (E_N)/eV	visible band/nm
F	1.8	4.10	395
Cl	6.2	2.83	475
Br	3.0	2.74	550
I	0.1	2.21	630
H	1.0	2.20	350−500

with $Fe(CN)_6^{3-}$ with a bimolecular rate constant of 6.6×10^7 dm^3 mol^{-1} s^{-1}, as determined from the bleaching of $Fe(CN)_6^{3-}$ at 420 nm (Figure 4) (reaction 3).

$$[C_6H_6(OH)]^\bullet + Fe(CN)_6^{3-} \rightarrow C_6H_5OH + Fe(CN)_6^{4-} + H^+ \quad (3)$$

It is known that the one-electron oxidation of hydroxycyclohexadienyl type radicals by $Fe(CN)_6^{3-}$ yields the corresponding phenols.[13] The bimolecular rate constant value for the oxidation of the OH adduct of chlorotoluene has been determined to be in the range $(1.8-4.2) \times 10^7$ dm^3 mol^{-1} s^{-1}. Therefore, the bleaching of $Fe(CN)_6^{3-}$, observed on pulse radiolysis of benzene should be due to the oxidation of an OH adduct of benzene (reaction 3) by $Fe(CN)_6^{3-}$.

The different redox behavior of the transient species formed in neutral and acidic conditions supports the formation of different transient species on reaction of $^\bullet OH$ radicals with benzene. Although the position of the transient absorption band at 310 nm remained the same both in neutral and acidic solutions, and the band in the visible region is broad with low molar absorptivity ($\epsilon_{400} = 1.2 \times 10^3$ dm^3 mol^{-1} cm^{-1}), earlier pulse radiolysis studies on halogenated benzenes (C_6H_5X; X = F, Cl, Br, I) have clearly shown the formation of a distinct transient absorption band in the visible region (Table 1).[27] The band in the visible region is due to the solute radical cation, and the concentration of $HClO_4$ required for their formation was observed to depend on the electronegativity (E_N) of the halogen (Figure 5).[40] Except for fluorine, the concentration of $HClO_4$ required for the formation of solute radical cation increased linearly with the electronegativity of the halogen, thus supporting the formation of the benzene radical cation (Scheme 1). Fluorine behaves differently and may be due to strong electron withdrawing by the field inductive effect and the weak electron pair donating nature.[41]

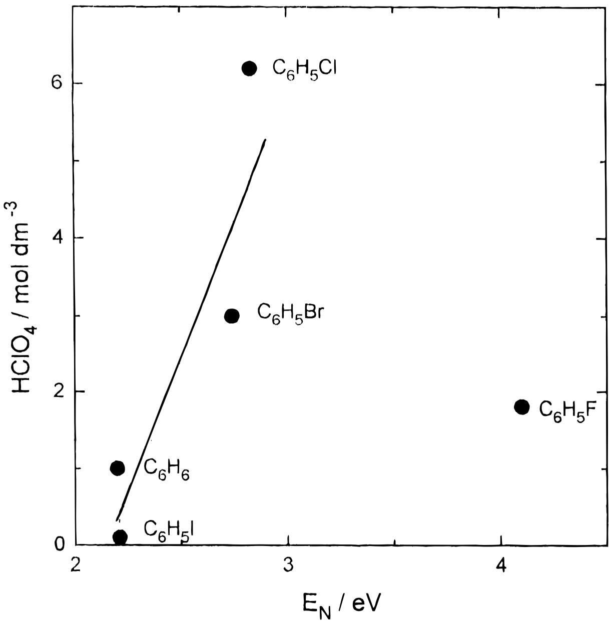

Figure 5. Variation of [$HClO_4$] required for the formation of the radical cation of halogenated benzenes with the electronegativity of the halogen.

γ-radiolysis of benzene in a glassy matrix at 77 K has shown the formation of transient absorption bands at 470 and 910 nm, which were assigned to the benzene radical cation.[2,29,30] On the other hand, chemical oxidation of benzene by antimony pentachloride produced the benzene radical cation with an absorption band at 445 nm.[42,43] A broad absorption in the 400−480 nm region observed on γ-radiolysis of benzene in perfluorocarbon polymer film at 77 K is also assigned to the benzene radical cation.[30] The absorption spectra of cation radicals are often compared with the photoelectron spectra of the parent molecule. Photoelectron spectroscopic data[30,44] on benzene in the vapor state show bands corresponding to the transition energy of 9.25, 11.49, 12.1, 13.8, and 14.59 eV. The transition between 9.25 and 12.1 eV corresponds to a photon energy of 435 nm. This is close to the peak at 400 nm. The transition between 9.25 and 13.8 eV has an energy equal to 273 nm. This is close to the observed transient optical absorption band at 310 nm. The small broad absorption band with a peak at 400 nm (Figure 2c) is close to the visible absorption band of the benzene radical cation reported in the literature.[2,29,30,41,42] The difference in the position of absorption bands formed on pulse radiolysis of aqueous solutions and photoelectron spectroscopic data are also observed for chlorobenzene and bromobenzene.[27c,27b] The difference in the position of the transient optical absorption band and the photoelectron spectroscopic data could be due to the fact that the transient optical absorption bands are from fully relaxed states, which might have undergone reorientation of the electrons and solvation of the cation.

4. Conclusions

The unambiguous assignement of the absorption spectrum of the benzene radical cation was not possible in the past mainly due to its high reactivity, which reduces the yield. The yield of the benzene radical cation is increased in highly acidic solutions. Although the transient absorption band at 310 nm, assigned to the benzene radical cation, matches that of the OH adduct and the broad absorption in the 350−500 nm regions with a peak at 400 nm has a very low molar absorptivity, the cationic nature of the transient species formed on reaction of $^\bullet OH$ radicals in highly acidic solution supports the formation of the benzene radical cation. The solute radical cation is a strong one-electron oxidant with oxidation potential in the range 2.1−2.4 V vs NHE.

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