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Electrochemical reductive cleavage of carbon–halogen bonds in 5-bromo-1,3-dichloro-2-iodobenzene

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Abstract—The electrochemical reduction of carbon–halogen bonds in 5-bromo-1,3-dichloro-2-iodobenzene follows quadratic activation–driving force relationship except in one of the carbon–chlorine bonds. The variation of the transfer coefficient with the electrode potential has been estimated using the voltammetric data coupled with the convolution analysis. The standard potentials pertaining to the reduction of carbon–halogen bonds are evaluated using the Marcus theory of outer sphere electron transfer.

1. Introduction

Electrochemical single electron transfer reactions constitute a frontier area of research[1] and the kinetics of these reactions can be analyzed using the Marcus–Hush theory of outer sphere electron transfer assuming the validity of the Born–Oppenheimer approximation. Electron transfer to an organic molecule (RX) is often accompanied by bond cleavage leading to a radical ($R^{\cdot}$) and an anion (X^{-}) occurring either in a stepwise manner (reaction 1) or a single elementary step (reaction 2).

$$RX + e^{-} \rightleftharpoons RX^{\cdot -}\ (E^{0}_{RX/RX^{\cdot -}}) \tag{1a}$$

$$RX^{\cdot -} \rightarrow R^{\cdot} + X^{-} \tag{1b}$$

$$RX + e^{-} \rightarrow R^{\cdot} + X^{-}\ (E^{0}_{RX/R^{\cdot}+X^{-}}) \tag{2}$$

Application of general electrochemical techniques yields the transfer coefficient and the forward electron transfer rate constant for the above reactions, but not the information about the standard potential (E^0) vis-à-vis the standard rate constant; since the dissociative electron transfer reactions are completely irreversible, E^0 values can not be obtained directly (for example, by cyclic voltammetry). However, the kinetic analysis of homogeneous redox catalysis of the electrochemical reduction leads to the determination of E^0.[2] An elegant method for the estimation of standard potentials of irreversible systems obeying a quadratic activation–driving force relationship was demonstrated in the dissociative reduction of perbenzoates.[3] The above methodology, making use of linear variation of transfer coefficient (α) with the electrode potential (E), was adopted in the electrochemical reduction of several organic[4–6] and biologically relevant molecules.[7] However, studies in this direction on the stepwise reductive cleavage reactions involving rapid decomposition of the anion radicals (especially aromatic compounds) are limited.

In this communication, we report the standard potentials of the irreversible reduction of aromatic carbon–halogen bonds in 5-bromo-1,3-dichloro-2-iodobenzene using the quadratic activation–driving force relationship. Convolution potential sweep voltammetry is the main tool for investigating the reaction kinetics, since, in contrast to homogeneous redox catalysis, the convolution approach allows one to obtain extensive data on the logarithmic electron transfer rate constant ($\ln k_{ET}$) versus electrode potential (E) variation. It has to be emphasized here that the present approach fails for systems involving linear variation of $\ln k_{ET}$ with E (Butler–Volmer kinetics)—an example of which also is demonstrated in the present study.

2. Experimental

The voltammetric studies were carried out in a single compartment electrochemical cell thermostated at 298 K, using the Bio Analytical Systems (BAS) 100A Electrochemical workstation. The working electrode was a glassy

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carbon disc (BAS) of 3 mm diameter while platinum foil ($2\ cm^2$) served as the counter electrode. The working electrode was polished with the alumina slurry (BAS) and ultrasonically rinsed prior to use. The electrochemical pretreatment was carried out in the background solution using several cycles at $0.05–1\ V\ s^{-1}$ in a wide potential range. Tetra *n*-butyl ammonium bromide (nBu$_4$NBr) (Fluka) was the supporting electrolyte and used as received. *N*,*N*′-dimethyl formamide (DMF) was initially distilled from anhydrous copper sulfate, then the distillate was again distilled from calcium hydride under reduced pressure and stored over 4 Å molecular sieves. Silver/silver ion (1 mM) electrode (BAS) was used as the quasi-reference electrode which was subsequently calibrated with the ferrocene/ferrocenium couple under identical conditions of solvent and supporting electrolyte. The background subtracted voltammograms were analyzed by the convolution approach, the experimental and computational details of which have been described earlier.[8] NMR spectra were recorded on Bruker Avance 400 spectrometer. UV–Vis spectrum was obtained with the Ocean Optics UV/Vis spectrometer.

5-Bromo-1,3-dichloro-2-iodobenzene was synthesized by the following procedure: 2,6-dichloroaniline was brominated by passing the vapours of bromine into a solution of 2,6-dichloroaniline in hydrochloric acid. The solid 4-bromo-2,6-dichloroaniline was filtered and purified by column chromatography (silica gel). 4-Bromo-2,6-dichloroaniline was then diazotized in hydrochloric acid (6 M) using aqueous sodium nitrite (6 M) and the resulting solution was slowly added to aqueous potassium iodide (5 M). When no gas was evolved, the crude product was filtered, washed with aqueous sodium hydroxide, subsequently with sodium metabisulphite and finally with water. The residue was purified by column chromatography (silica gel) using hexane as the eluent to give 5-bromo-1,3-dichloro-2-iodobenzene as white solid: Mp 67.8–68.7 °C (literature:[9] 67.5–68.2 °C); ^{1}H NMR (400 MHz, CDCl$_3$, TMS as internal standard) δ 7.48 (2H, s); ^{13}C NMR (100 MHz, CDCl$_3$) δ 102.41, 122.36, 129.89, 141.33; UV–Vis (CHCl$_3$) broad band centered at 300 nm. The compound was crystallized in hexane (colorless crystals) for the electrochemical studies and the crystal structure confirms the identity of the compound[†].

3. Results and discussion

Halobenzenes (RX) undergo irreversible electron transfers at the electrode surface and are capable of hosting transitorily the incoming electron in their π^* orbitals leading to the radical anions ($RX^{\bullet -}$) (reaction 1a). The radical anions readily undergo decomposition with a first order rate constant greater than $10^4\ s^{-1}$ to neutral radicals ($R^{\bullet}$) and halide ions (X^-) (reaction 1b).[10] The dissociation of the radical anion may be viewed as an intramolecular dissociative single-electron transfer from the π^* orbital to the σ^* orbital of the carbon–halogen bond.[11] Interestingly, the neutral radicals are easier to reduce than the parent halobenzenes and immediately undergo a second electron transfer to form R^-. However, the characteristic features of the reduction wave of halobenzene are solely governed by the kinetics of the first electron transfer. R^- abstracts a proton either from the solvent or the supporting electrolyte to give the hydrocarbon RH and it was observed that several halobenzenes and other aromatic halides upon electrolysis yielded 100% of RH.[10] A recent investigation, involving in situ electrochemical-NMR spectroscopy,[12] has revealed that the aryl anion abstracts a proton preferably from the solvent rather than the supporting electrolyte. It is worth mentioning here that the hydrocarbon RH is reducible and, in fact, a second wave is observed in some cases before the background discharge.[10] However, in most cases, the reduction wave of RH is suppressed by the background discharge current of the supporting electrolyte.

Figure 1 shows the cyclic voltammogram pertaining to the reduction of 5-bromo-1,3-dichloro-2-iodobenzene at the glassy carbon electrode in DMF containing 0.1 M nBu$_4$NBr as the supporting electrolyte. The reduction waves a, b, c and d represent, respectively, the two-electron reduction of carbon–iodine (C–I), carbon–bromine (C–Br) and two carbon–chlorine (C–Cl (1) and C–Cl (2)) bonds. This assignment follows from the fact that the carbon–halogen bonds are susceptible to reduction in the order of: C–I > C–Br > C–Cl > C–F. Each wave represents the hydrogenolysis of a carbon–halogen bond finally leading to the formation of benzene and hence an overall consumption of eight electrons in a single voltammetric cycle. The voltammogram B shows the reduction waves of 1,3-dichlorobenzene which corresponds to the peaks c and d of the voltammogram A. The π^* level of 5-bromo-1,3-dichloro-2-iodobenzene being comparatively lower than the monosubstituted benzene is proved by the fact that the reduction potential of carbon–iodine bond (wave a) is ca. 336 mV more positive than that of iodobenzene. A similar behaviour also arises for the carbon–bromine bond, the reduction potential of which is ca. 486 mV more positive than that of bromobenzene. However, the peak potential of wave d corresponds to that of chlorobenzene.[10] All the waves remain irreversible even at a scan rate of $2000\ mV\ s^{-1}$, indicating that the life time of the radical anion is less than 10^{-4} s. The peak currents of the waves a, b, c and d are proportional to the square root of the sweep rate. The transfer coefficient of the reduction of carbon–halogen bond can be calculated from the peak width measurements (Eq. 3) and the values are listed for various carbon–halogen bonds in Table 1.

$$\alpha = \frac{1.856RT}{F}\frac{1}{(E_{P/2} - E_P)} \tag{3}$$

The α values close to or greater than 0.5 are expected for stepwise mechanism. However, this is not an absolute criterion[3] and our systematic study has revealed that the reduction of carbon–iodine bond, for which the α value is less than 0.5, indeed follows a stepwise mechanism.[13]

[†] Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 231991. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

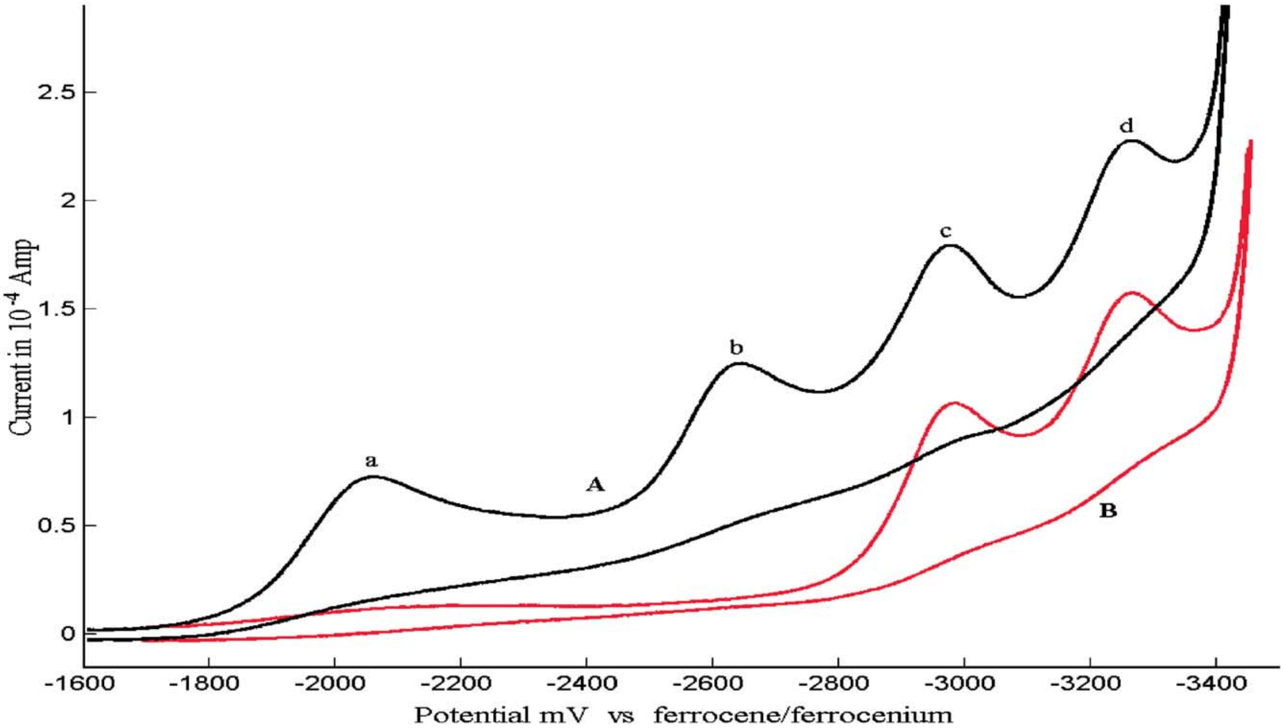

Figure 1. Cyclic voltammograms of (A) 5-bromo-1,3-dichloro-2-iodobenzene and (B) 1,3 dichlorobenzene in DMF/0.1 M $n\mathrm{Bu_4NBr}$ at glassy carbon electrode. Scan rate: 200 mV s^{-1}; temperature: 298 K.

3.1. Convolution analysis

In order to analyze the thermodynamic and kinetic behaviour of the electron transfer, it is essential to deduce the electron transfer rate constant as a function of potential. In this respect, convolution voltammetry is a powerful electrochemical tool since it employs all the data points of the voltammetric wave rather than the peak characteristics alone.[3] The convolution current (I) is related to the actual current (i) through the convolution integral[14] (Eq. 4).

$$I = \frac{1}{\sqrt{\pi}}\int_0^t \frac{i(u)}{(t-u)^{1/2}}\,\mathrm{d}u \qquad (4)$$

The plot between I versus E is sigmoidal in shape with the plateau being reached when the applied potential is sufficiently negative. Under this condition, I reaches its limiting value I_L defined as in Eq. 5

$$I_L = nFAD^{1/2}C_b \qquad (5)$$

where D is the diffusion coefficient and C_b, the bulk concentration. Figure 2 shows the convolution potential sweep voltammogram of the reduction of 5-bromo-1,3-dichloro-2-iodobenzene at a scan rate of 200 mV s^{-1}. In the case of closely spaced waves I_L was obtained at a potential at which the minimum occurs in the plot of derivative of the convolution current at the plateau region. The logarithmic analysis of the convolution current in conjunction with the voltammetric current yields the heterogeneous electron transfer rate constant[14] as in Eq. 6.

$$\ln k_{ET} = \ln D^{1/2} - \ln\frac{I_L - I(t)}{i(t)} \qquad (6)$$

Figure 3 depicts the variation of $\ln k_{ET}$ with E at various scan rates for the reduction of C–I, C–Br, C–Cl (1) and C–Cl (2) bonds. In the cases of C–I, C–Br and C–Cl (2), the variations are parabolic, obeying the quadratic activation (ΔG^*)–driving force (ΔG^0) relationship (Eq. 7).

$$\Delta G^* = \frac{(\Delta G^0)^2}{16\Delta G_0^*} + \frac{\Delta G^0}{2} + \Delta G_0^* \qquad (7)$$

However, in the reduction of C–Cl (1) bond, the variation of $\ln k_{ET}$ with E is linear. In this case the transfer coefficient is constant, conforming to Butler–Volmer kinetics (α obtained from the slope of the plot (Eq. 9) equals that obtained from

Table 1. Electrochemical reduction behaviour of carbon–halogen bonds in 5-bromo-1,3-dichloro-2-iodobenzene

Carbon–halogen bond	Transfer coefficient from peak width measurements	Transfer coefficient from the Eq. 9	$E^0_{\mathrm{RX/RX^{\cdot-}}}$ in mV versus SCE	$E^0_{\mathrm{RX/RX^{\cdot-}}}$ for halobenzenes in mV versus SCE from Ref. 17
C–I	0.331	—	−1401	−2240 (iodobenzene)
C–Br	0.451	—	−2124	−2440 (bromobenzene)
C–Cl (1)	0.659	0.667	—	—
C–Cl (2)	0.604	—	−2856	−2780 (chlorobenzene)

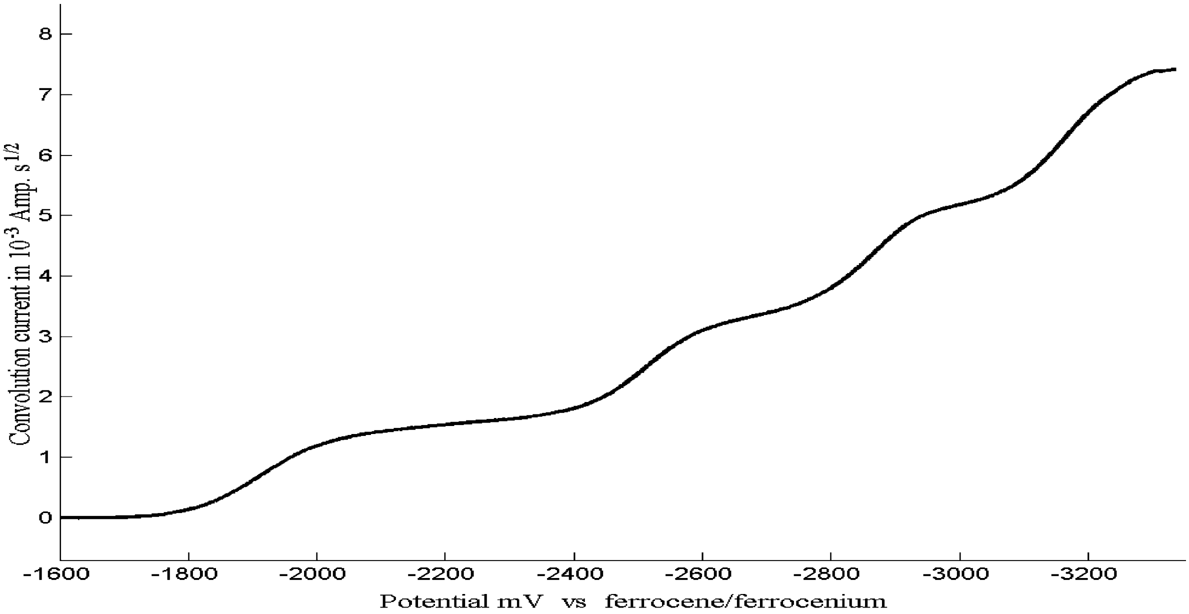

Figure 2. Convolution potential sweep voltammogram of background subtracted voltammetric curve for the reduction of 5-bromo-1,3-dichloro-2-iodobenzene in DMF containing 0.1 M nBu$_4$NBr at the glassy carbon electrode. Scan rate: 200 mV s^{-1}; temperature: 298 K.

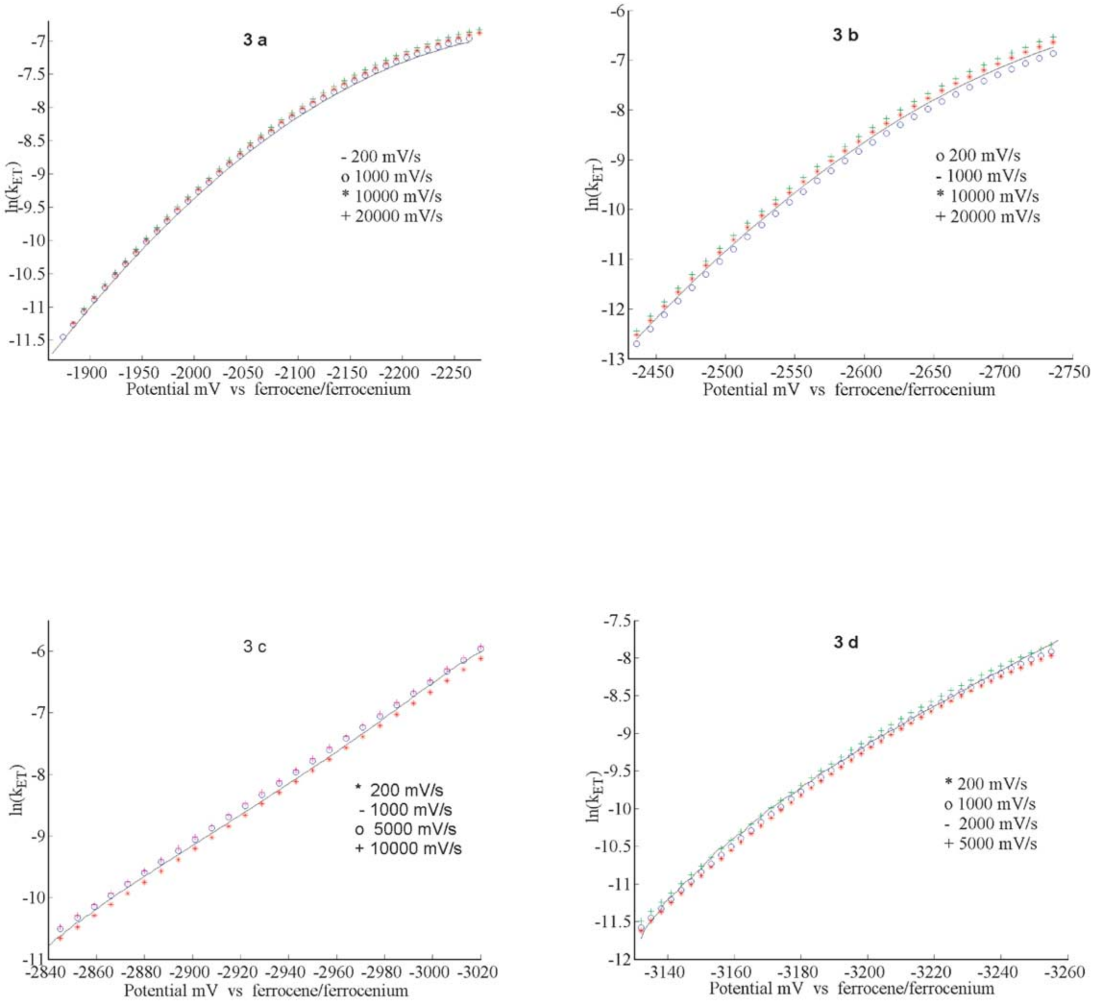

Figure 3. Potential dependence of logarithmic heterogeneous electron transfer rate constant for the reduction of (a) carbon–iodine bond (b) carbon–bromine bond (c) carbon–chlorine (1) bond and d) carbon–chlorine (2) bond at various scan rates.

the peak width measurements (Table 1)). It may be argued that a parabola with a small curvature would also fit the experimental ln k_{ET} versus E plot for the reduction of C–Cl (1) bond. However, this possibility can be excluded, since the ln k_{ET} versus E plot is too linear to be accounted for within the purview of a stepwise mechanism. Furthermore, α is too large to be accounted for by the theory within the framework of a concerted pathway.

3.2. Standard potential

The rate of change of activation energy (ΔG^*) with respect to the driving force (ΔG^0), yields the transfer coefficient as Eq. 8

$$\alpha = \frac{\partial \Delta G^*}{\partial \Delta G^0} = 0.5 + \frac{\Delta G^0}{8\Delta G_0^*} \tag{8}$$

Experimentally α is estimated from the derivative of ln k_{ET} versus E plot using Eq. 9

$$\alpha = -\frac{RT}{F}\frac{\mathrm{d}\ln k_{\mathrm{ET}}}{\mathrm{d}E} \tag{9}$$

wherein the symbols R, T and F assume the usual significance. Figure 4 shows the variation of α with E at various scan rates for the reduction of C–I, C–Br and C–Cl (2) bonds. Since the variation of ln k_{ET} with E is parabolic, α varies linearly with E. As implied by Eq. 8, most theoretical models for outer sphere or dissociative electron transfers predict that α should be 0.5 at zero driving force[15,16] ($\Delta G^0 = F(E - E^0) = 0$). From the linear α versus E variation, $E^0_{\mathrm{RX/RX^{\cdot-}}}$ of the reduction of respective carbon–halogen bonds can be estimated as the potential at which α becomes 0.5.[4] Table 1 shows $E^0_{\mathrm{RX/RX^{\cdot-}}}$ values for the reduction of C–I, C–Br and C–Cl (2) bonds obtained using the above methodology. Table 1 also provides $E^0_{\mathrm{RX/RX^{\cdot-}}}$ values for the reduction of iodobenzene, bromobenzene and chlorobenzene for comparison.[10,17] The standard potentials of the reduction of bromobenzene and chlorobenzene were determined through the kinetic analysis of homogeneous redox catalysis of the electrochemical reduction by Saveant et al.[10] and that of the reduction of iodobenzene was obtained in an approximate way using the standard free energy of anion radical cleavage.[17]

The standard potentials of the reduction of C–I and C–Br are 839 and 316 mV more positive than those for the reduction of iodobenzene and bromobenzene, respectively (Table 1). This is consistent with the fact that the energy of the π* orbital of the ring increases with the elimination of each halogen, viz. lowest at the first wave and highest at the fourth wave, which is reflected in the standard potentials of the reduction of respective carbon–halogen bonds. Even though α is substantially lower in the reduction of C–I, the energy of the π* orbital of the ring is low enough to trap the unpaired electron before it

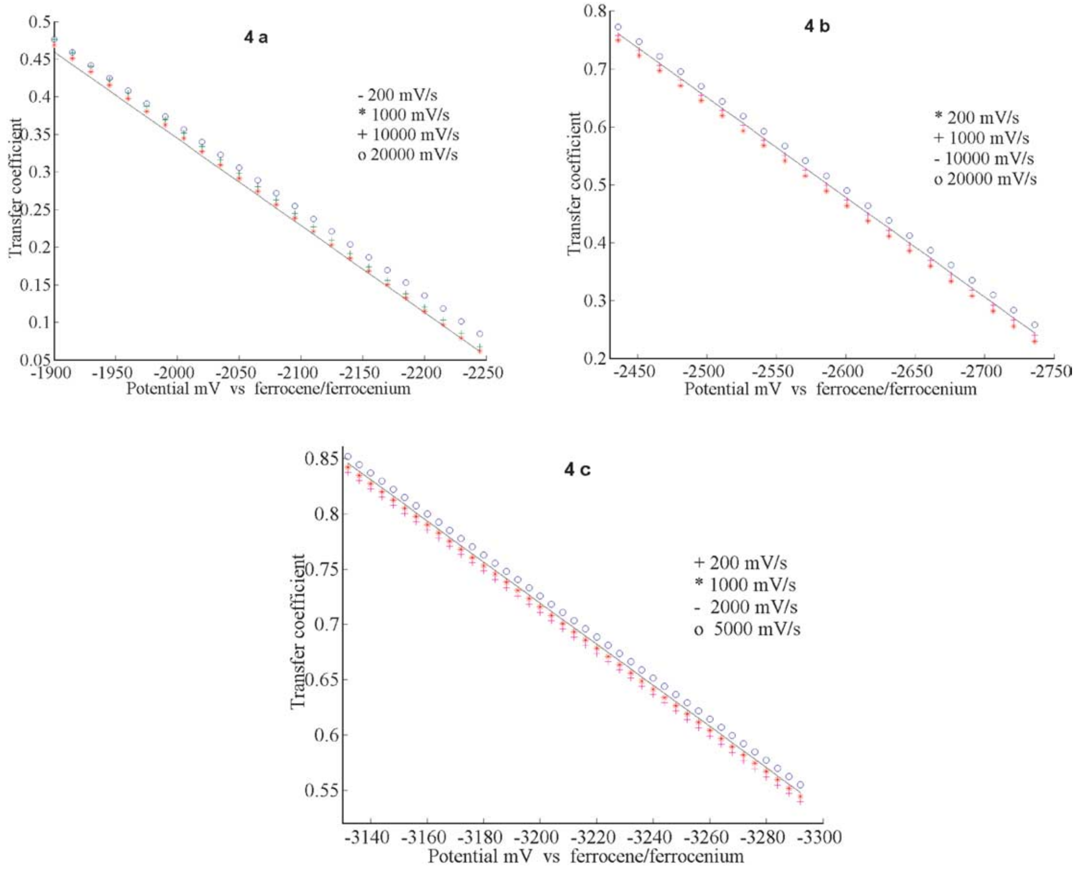

Figure 4. Variation of apparent transfer coefficient with electrode potential at various scan rates for the reduction of (a) carbon–iodine bond (b) carbon–bromine bond and (c) carbon–chlorine (2) bond.

dissociatively reduces the C–I bond in a successive step.[13] A difference between the $E^0_{RX/RX^{\cdot-}}$ for the reduction of C–Cl (2) and that for the reduction of chlorobenzene may be attributed to the different supporting electrolyte (nBu$_4$NI) and working electrode (mercury) employed in the earlier study.[10] Further, in our estimation of standard potentials, double layer corrections have not been applied; however it has been demonstrated[18] that the standard potential calculations carried out incorporating the double layer effects amounts to a maximum difference of only 0.06–0.07 V. This fact is particularly significant, since good experimental data are obtained from the glassy carbon electrode—the double layer properties of which are unknown.

4. Summary

The electrochemical reduction of 5-bromo-1,3-dichloro-2-iodobenzene results in four irreversible voltammetric waves consuming eight electrons in a single cycle. The reduction of C–I, C–Br and C–Cl (2) bonds lead to parabolic $\ln K_{ET}$ versus E plots obeying quadratic activation–driving force relationship. The analysis employing the Marcus theory of outer sphere electron transfer in conjunction with the convolution approach yields standard potentials of the reduction of carbon–halogen bonds in 5-bromo-1,3-dichloro-2-iodobenzene except in one of the carbon–chlorine bonds wherein the reduction follows Butler–Volmer kinetics.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tet.2004.09.020

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