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Cleavage of an aromatic carbon–heteroatom bond in a single step or successive steps?—A mechanistic distinction in the reduction of 5-bromo-1,3-dichloro-2-iodobenzene

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Abstract—The electrochemical reductive cleavage of the carbon–iodine bond in 5-bromo-1,3-dichloro-2-iodobenzene has been analyzed from the mechanistic point of view employing the Marcus theory of heterogeneous outer sphere electron transfer. The variation of the electrochemical transfer coefficient with potential has been estimated from the cyclic and convolution voltammetric studies. The comparison of the experimental reorganization energy with the theoretical predictions has revealed the existence of the radical anion of 5-bromo-1,3-dichloro-2-iodobenzene as a transient species.

1. Introduction

Homogeneous or heterogeneous electron transfer accompanied by the cleavage of a bond may occur via two possible pathways, viz. (i) by involving a transient ion radical (reaction 1) or (ii) by simultaneous electron transfer and bond cleavage (reaction 2) leading to the radical and ion:

Stepwise:

$$RX + e^- \leftrightarrows RX^{\bullet -} \tag{1a}$$

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

Concerted:

$$RX + e^- \rightarrow R^\bullet + X^- \tag{2}$$

The distinction between these two mechanistic pathways has been a subject of interest in recent times.[1,2] Molecules involving low lying orbitals (π^* orbitals) are capable of hosting temporarily the incoming electron leading to a stable radical anion. In this respect, the stepwise bond cleavage is favored for several aromatic halides and the activation-driving force in these cases follows a quadratic relationship.[2] Halobenzenes, which constitute the simplest examples in this context, on reduction, lead to the cleavage of the carbon–halogen bond involving the initially generated radical anion.[3] Among carbon–halogen bonds, the carbon–iodine bond is highly susceptible to reduction and undergoes a peculiar mechanistic transition as a function of the potential scan rate, vis-à-vis, the driving force of the electrochemical reduction.[3,4] In this Letter, we report the electrochemical reduction of a polyhalobenzene, viz. 5-bromo-1,3-dichloro-2-iodobenzene and deduce whether a concerted or stepwise reduction of the carbon–iodine bond is involved.

2. Mechanistic diagnosis

Figure 1 shows the cyclic voltammogram pertaining to the reduction of 5-bromo-1,3-dichloro-2-iodobenzene at glassy carbon electrodes in DMF containing 0.1 M $n\mathrm{Bu_4NBr}$ as the supporting electrolyte. The waves a, b, c, and d represent the two-electron reduction of carbon–iodine, carbon–bromine, and two carbon–chlorine bonds, respectively[4] (the voltammogram B shows the

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Keywords: 5-Bromo-1,3-dichloro-2-iodobenzene; Reductive cleavage; Concerted mechanism; Stepwise mechanism; Reorganization energy; Transfer coefficient.

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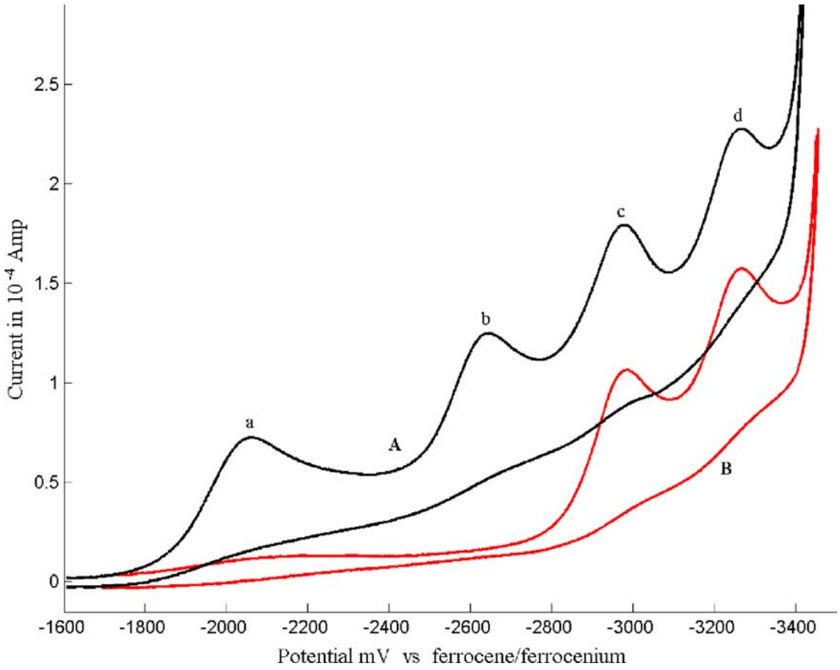
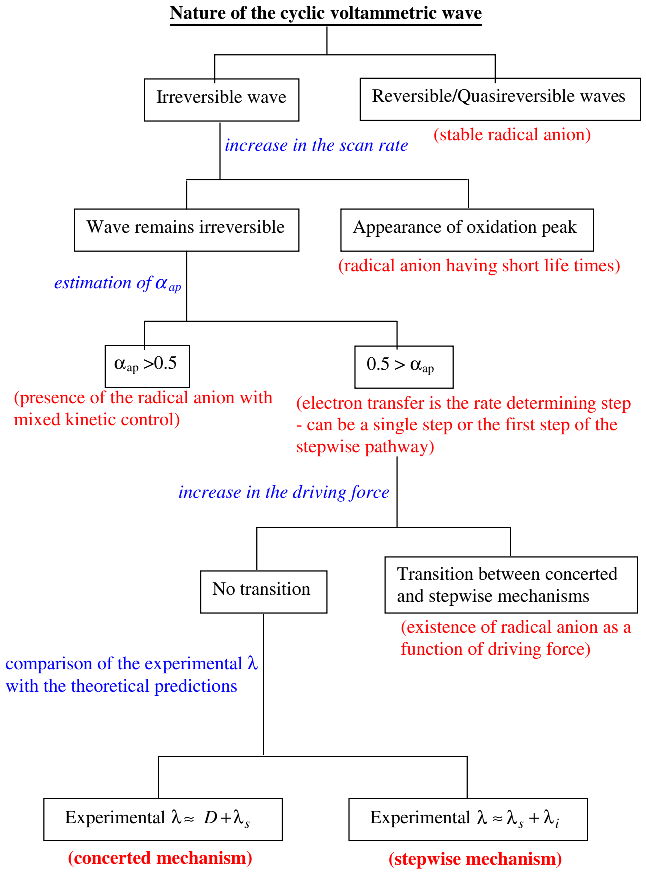


Figure 1. Cyclic voltammograms of 5-bromo-1,3-dichloro-2-iodobenzene (A) and 1,3 dichlorobenzene (B) in DMF containing 0.1 M $n\mathrm{Bu_4NBr}$ at the glassy carbon electrode. Scan rate: 200 mV s^{-1}; Temperature: 298 K.

reduction waves of 1,3-dichlorobenzene, which correspond to the peaks c and d of the voltammogram A). The mechanistic diagnosis of the reduction of the carbon–iodine bond was carried out according to Scheme 1. As can be noted from Figure 1, all the waves are irreversible, indicating either the absence of or a short lived radical anion of 5-bromo-1,3-dichloro-2-iodobenzene. An increase in the scan rate to even 2000 V s^{-1} did not yield an oxidation wave of the radical anion and hence the decomposition of the radical anion (reaction 1b) could be very fast with a lifetime smaller than 10^{-4} s. The next step involves the determination of the apparent transfer coefficient (α_{ap}) whose value may allow discrimination between the two mechanisms.[5] In this respect, the convolution voltammetry lends itself utilizing all the information contained in a single current–potential curve instead of that involving only the peak values.[6] Furthermore, the form of the kinetic law need not be known a priori and the method is particularly useful in the study of electron transfer reactions involving fast bond cleavages. Using the logarithmic analysis of the convolution wave, the apparent rate constant (which varies quadratically with the potential (E)) was determined[7] and subsequent differentiation yielded α_{ap} as a function of potential (Fig. 2).

As can be seen from Figure 2, α_{ap} equals 0.272 at the peak potential (−2063 mV versus ferrocene/ferrocenium; scan rate: 200 mV s^{-1}). This is quite interesting since, when α_{ap} reaches 0.5 or less, the rate determining step is the electron transfer, which may be either the initial electron transfer of the stepwise pathway (reaction 1a) or the dissociative electron transfer of the concerted pathway (reaction 2). Under such conditions, as demonstrated elsewhere,[3] the observation of a transition between stepwise and concerted pathways with increase in the driving force (scan rate) allows an unambiguous distinction between the two pathways. However, in our



Scheme 1. Diagnosis criteria for the distinction between concerted and stepwise mechanisms of reductive cleavage of organic halides.

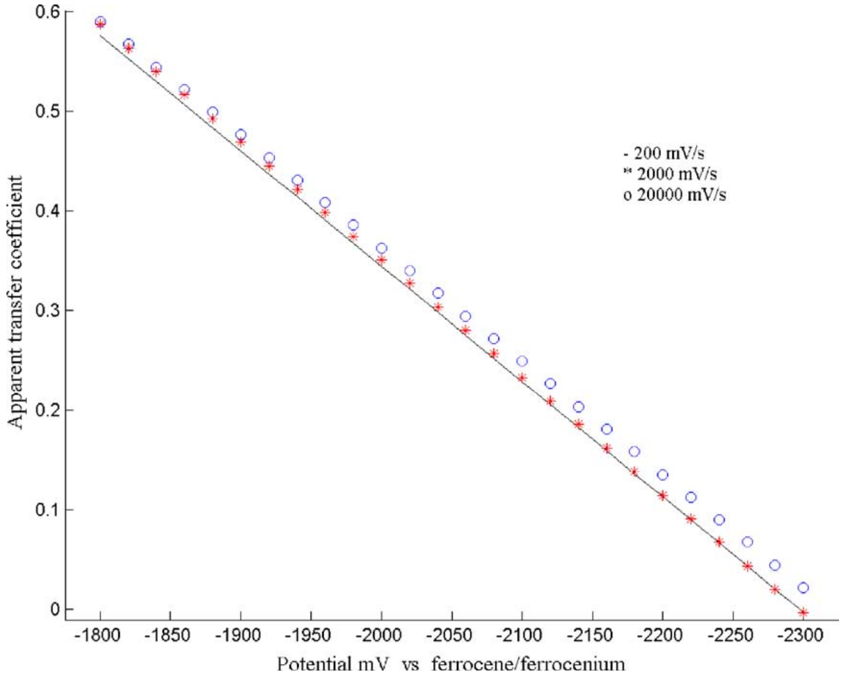


Figure 2. Variation of the apparent transfer coefficient with potential at various scan rates.

case, α_{ap} does not increase appreciably with the logarithmic scan rate and hence no mechanistic transition occurs.

3. Reorganization energy

In this instance, it is worth noting two prevailing contradictory situations, viz. (i) the π^* level of the ring in the polyhalobenzene being comparatively lower than the monosubstituted halobenzene, accommodating an incoming electron should be facile leading to an enhanced stabilization of the radical anion, and (ii) on the other hand, the value of α_{ap} points to a concerted pathway (which need not always be the case[5]). To distinguish between these two possibilities, the reorganization energy (λ) was evaluated from the α_{ap} versus E plot and compared with the theoretical predictions for concerted and stepwise pathways, respectively. The equation for the linear variation in Figure 2 can be formulated from the Marcus–Hush theory of outer sphere electron transfer[8,9] and its extension to the dissociative processes.[10] The theory (the quadratic law) relates the activation barrier (ΔG^*) to the driving force (ΔG^0; $\Delta G^0 = F(E - E^0)$) of the reaction as

$$\Delta G^* = \frac{(\Delta G^0)^2}{16\Delta G_0^*} + \frac{\Delta G^0}{2} + \Delta G_0^* \tag{3}$$

wherein ΔG_0^* is the intrinsic barrier and is proportional to λ, viz.

$$\Delta G_0^* = \frac{\lambda}{4} \tag{4}$$

λ is contributed by two independent terms, viz. for the concerted pathway

$$\lambda = D + \lambda_s \tag{5}$$

and in the case of stepwise pathway

$$\lambda = \lambda_s + \lambda_i \tag{6}$$

D is the bond dissociation energy of the cleaving bond. λ_s and λ_i represent respectively, the solvent and inner reorganization energies. Differentiation of Eq. (3) with respect to ΔG^0 and substituting for ΔG^0 and ΔG_0^* yields α as

$$\alpha = 0.5 + \frac{F(E - E^0)}{2\lambda} \tag{7}$$

where E^0 is the standard potential for the concerned pathway. From the above equation, the slope of the plot α versus E becomes $\frac{F}{2\lambda}$ and the mean slope of the straight lines in Figure 2 is $1.159\,\mathrm{V}^{-1}$ yielding the experimental λ as 0.431 eV. The bond dissociation energy D of the carbon–iodine bond is 2.835 eV,[11] which is several folds higher than the experimental λ (Eq. 5, not to mention the contribution from λ_s). Hence the possibility of the concerted mechanism in the reduction of carbon–iodine bond can be excluded. λ_s in the Eq. 6 can be computed from the Marcus equation for solvent reorganization. There are several versions of the Marcus equation[12,13] and none of them yielded λ_s greater than 0.4 eV (λ_i can be neglected[12] in view of its meager contribution to λ). Since the experimental λ is consistent with λ_s, it can be inferred that the radical anion of 5-bromo-1,3-dichloro-2-iodobenzene is indeed a reaction intermediate. In view of the relatively strong electron-accepting property of the halogens, the π^* energy of the ring is lower than the iodobenzene and hence the more facile accommodation of a negative charge occurs rather than the direct electron transfer to σ^* orbital of the carbon–iodine bond. This is reflected in the peak potential of the first wave, which is ca. 336 mV more positive to that of iodobenzene.[3]

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