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The Electrochemical Cleavage of Carbon-Halogen Bonds of Haloferrocenes

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Synopsis. The cyclic voltammetric studies for haloferrocenes, FcX (X=Cl, Br, and I), in etylene glycol dimethyl ether at −45 °C have been reported. The cyclic voltammogram and the absorption spectrum of the solution after the exhaustive controlled-potential reduction for the reduction step of haloferrocene show a quantitative formation of ferrocene and a cleavage of the carbon-halogen bond of haloferrocene.

A vast amount of information regarding the organic chemistry of ferrocene (FcH) has been reported since its discovery.[1] The chemistry of ferrocene is similar to that of aromatic hydrocarbons. For example, ferrocene very readily undergoes Fridel-Craft acylation, alkylation, metalation by butyllithium.

It is known that FcH and its derivatives can be oxidized to ferrocenium cation (FcH$^+$) electrochemically as well as chemically.[2] On the other hand, Mugnier *et al.* and we ourselves have reported that ferrocene can be reduced quasireversibly in etylene glycol dimethyl ether (DMeE) at −45 °C, and that a stable ferrocene anion (FcH$^-$) exists for a few minutes.[3,4] Only a few cases of the electrochemical reduction of ferrocene dirivatives have been reported.[5] Such electron-rich anions are interesting in their reactivity.[6] The present note will deal with voltammetric and controlled-potential electrolytic studies of haloferrocenes undertaken in order to examine the mechanism of the reduction process.

Experimental

Iodoferrocene (FcI) was prepared by the reaction of (chloromercurio) ferrocene with iodine.[6] Chloroferrocene (FcCl) and bromoferrocene (FcBr) were prepared by the halogen-exchange reaction of FcI with copper(I) salts.[7] These complexes were purified by sublimation and identified on the basis of their melting points and elemental analyses on C, H, N, and halogen. The preparation of the test solutions and the procedures for the electrochemical measurements has been described previously.[4] Chloroferrocene: mp 56—56.5 °C (lit,[7] 56—56.5 °C). Found: C, 53.85; H, 4.04; N, 0.00, Cl, 16.78%. Calcd for $C_{10}H_9ClFe$: C, 54.47; H, 4.11; N, 0.00; Cl, 16.08%. Bromoferrocene: mp 30.5—31 °C (lit,[9] 30—31 °C). Found: C, 44.84; H, 3.32; N, 0.00; Br, 31.78%. Calcd for $C_{10}H_9BrFe$: C, 45.33; H, 3.42; N, 0.00; Br, 30.16%. Iodoferrocene: mp 48—49 °C (lit,[10] 49—49.5 °C). Found: C, 38.40; H, 2.84; N, 0.00; I, 41.23. Calcd for $C_{10}H_9IFe$:C, 38.50; H, 2.91; N, 0.00; I, 40.68%.

Results and Discussion

Figure 1 shows a cyclic voltammogram for 0.6 mM (mmol dm^{-3}) of FcCl in 0.2 M tetrabutylammonium perchlorate (TBAP) in DMeE, recorded at −45 °C with a scan rate of 0.2 V s^{-1}. It exhibits one reversible one-electron step at +0.04 V *vs.* Ag/AgNO$_3$(sat.), and two reduction steps at −3.35 V (reduction peak potential, E_{pc}) and −3.56 V, where potentials are indicated in terms of the potential at the midpoint between the cathodic peak potential (E_{pc}) and the anodic one (E_{pa}), $(E_{pa}+E_{pc})/2$, except for the case of the first reduction step. The reversal current peak of the step at −3.35 V can not be observed, even with a scan rate of 2 V s^{-1}. The step at −3.56 V was quasireversible. After the cathodic sweep was reversed at a potential less than the first reduction step, a small reversible one-electron oxidation step appeared at −0.13 V (Fig. 1-b). The half-wave potentials and the reversibilities of the second reduction and small oxidation steps were the same as those for the reduction and oxidation steps of FcH under the same conditions (Table 1). At room temperature, the first reduction step was observed at −3.28 V (E_{pc}), but the second reduction step was masked by the ultimate current rise. Similar voltammograms were obtained for FcBr and FcI. Table 1 lists the voltammetric results of these compounds. The first reduction peak potentials become more positive in the order of substituents, I>Br>Cl. This order agrees with that of the reactivities of haloferrocenes for photosubstitution.[11]

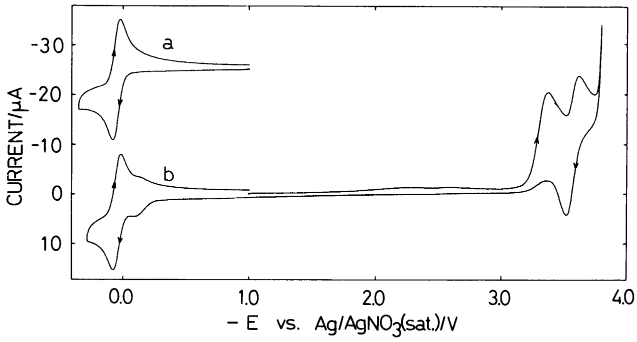

Fig. 1. Cyclic voltammogram of 0.6 mM chloroferrocene in 0.2 M TBAP–DMeE at −45 °C. Scan rate 0.2 V s^{-1}.

Table 1. The voltammetric data of chloro-, bromo-, and iodo- ferrocenes in 0.2 M TBAP-DMeE at −45 °C. scan rate: 0.2 V s^{-1}

Compound	$E^{\mathrm{ox}}_{1/2}$ a,b	$E^{\mathrm{ox}}_{1/2}$ a,c	$E^{\mathrm{red}}_{\mathrm{p}}$ a,d	$E^{\mathrm{red}}_{1/2}$ a,e
Chloroferrocene	+0.04	−0.13	−3.35	−3.56
Bromoferrocene	+0.03	−0.13	−3.29	−3.57
Iodoferrocene	+0.01	−0.13	−3.23	−3.57
Ferrocene		−0.13		−3.58

a) *Vs.* Ag/AgNO$_3$(sat.) in V. b) Half-wave potential of the oxidation step in V. c) Half-wave potential of the small oxidation step after cathodic sweep in V. d) Peak potential of the first reduction step in V. e) Half-wave potential of the second reduction step in V.

An exhaustive controlled potential reduction of 2.0 mM FcCl in 0.5 M TBAP–DMeE with a Pt electrode held at −3.4 V at room temperature was undertaken in order to study the product for the reduction of FcCl. The solution of the reduced product was yellow. A cyclic voltammogram of this solution agreed with that of ferrocene under the same conditions. The peak current of this oxidation step showed that FcCl is quantitatively converted into ferrocene. The absorption spectrum of this solution also agreed with that of ferrocene.

Consequently, the electrochemical reduction of haloferrocene (FcX) may be said to result in the cleavage of the carbon–halogen bond and may proceed through the following process in the same manner as aromatic hydrocarbons:[12]

$$\begin{aligned} \mathrm{FcX} &\overset{+e}{\rightleftharpoons} \mathrm{FcX^-} \\ &\longrightarrow \mathrm{Fc\cdot} + \mathrm{X^-} \\ \mathrm{Fc\cdot} &\xrightarrow{+e} \mathrm{Fc^-} \\ &\xrightarrow{+H^+} \mathrm{FcH} \end{aligned}$$

Such a quantitative formation of the ferrocenyl radical can be used in the preparation of ferrocene derivatives in place of the photolytic method.[11,13]

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