Direct Reduction of 1-Bromo-6-chlorohexane and 1-Chloro-6-iodohexane at Silver Cathodes in Dimethylformamide

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ABSTRACT

Cyclic voltammetry and controlled-potential (bulk) electrolyses have been employed to probe the electrochemical reductions of 1-bromo-6-chlorohexane and 1-chloro-6-iodohexane at silver cathodes in dimethylformamide (DMF) containing 0.050 M tetra-n-butylammonium tetrafluoroborate (TBABF$_4$). A cyclic voltammogram for reduction of 1-bromo-6-chlorohexane shows a single major irreversible cathodic peak, whereas reduction of 1-chloro-6-iodohexane gives rise to a pair of irreversible cathodic peaks. Controlled-potential (bulk) electrolyses of 1-bromo-6-chlorohexane at a silver gauze cathode reveal that the process involves a two-electron cleavage of the carbon–bromine bond to afford 1-chlorohexane as the major product, along with 6-chloro-1-hexene, n-hexane, 1-hexene, and 1,5-hexadiene as minor species. In contrast, bulk electrolyses of 1-chloro-6-iodohexane indicate that the first voltammetric peak corresponds to a one-electron process, leading to production of a dimer (1,12-dichlorododecane) together with 1-chlorohexane and 6-chloro-1-hexene as well as 1-hexene and 1,5-hexadiene in trace amounts. At potentials corresponding to the second cathodic peak, reduction of 1-chloro-6-iodohexane is a mixture of one- and two-electron steps that yields the same set of products, but in different proportions. Mechanistic schemes are proposed to explain the electrochemical behavior of both 1-bromo-6-chlorohexane and 1-chloro-6-iodohexane.

1. Introduction

In a recent publication [1] from our laboratory, the electro-chemical reduction of a pair of dibromoalkanes, namely 1,2- and 1,6-dibromohexane, at silver cathodes in dimethylformamide was examined. Cyclic voltammograms for each compound exhibit a single irreversible peak, but the cathodic peak potentials are significantly different. Moreover, for identical concentrations of each compound, the cathodic peak current for 1,2-dibromohexane is one half of that for 1,6-dibromohexane, an observation directly related to the number of electrons associated with reduction of each species and thus with the mechanism for reduction of each substrate. Whereas only one product (1-hexene) is formed via bulk electrolysis of 1,2-dibromohexane, a mixture of five different species (1-hexene, n-hexane, 1,5-hexadiene, 5-hexen-1-ol, and n-dodecane) can arise from the controlled-potential reduction of 1,6-dibromohexane. In hindsight, it is surprising that the electrochemical behavior of no other dihalohexane at a silver cathode has been investigated. However, in relatively recent work, Simonet [2] has probed the electrochemical reduction of 1,3-dibromopropane at silver cathodes in dimethylformamide containing tetra-n-butylammonium salts; this compound was found to undergo two-electron reduction to afford a diradical that undergoes polymerization, as well as cyclization to yield cyclopropane. Aside from these two publications, we are not aware of any other work that deals with reduction of α,ω-dihaloalkanes at a silver cathode.

In much earlier work, our laboratory carried out a series of studies [3–7] that involved the direct reduction of a family of α,ω-dihaloalkanes (ranging from compounds with n-propyl to n-decyl moieties and with identical or dissimilar halogens) at carbon cathodes in dimethylformamide. Whereas bulk electrolyses of various α,ω-dihalopropanes led almost exclusively to the formation of cyclopropane [3], the α,ω-dihalobutanes and α,ω-dihalopentanes afforded the corresponding cycloalkanes in modest yield [4,5]. On the other hand, preparative-scale

electrolyses of α,ω-dihalogenated hexanes, octanes, and decanes produced no carbocyclic products, but only mixtures of straight-chain alkanes and alkenes, along with some dimeric species arising from radical-coupling reactions [6,7].

In the last two decades, there has been considerable interest in the use of silver cathodes to investigate electron-transfer events centered on the electrochemical reduction of carbon–halogen bonds. Investigations have focused on (a) mechanistic features of these processes, (b) applications in the field of electrosynthesis, and (c) uses of electrochemical reductions at silver electrodes for the dehalogenation of environmental pollutants. These studies have revealed the catalytic ability of silver as a cathode for the reductive cleavage of carbon–halogen bonds at much less negative potentials than for other electrodes such as glassy carbon or mercury [8]. Without being encyclopedic, but hoping to provide some guidance to interested readers, we summarize briefly in the next paragraph some recent literature that identifies both important contributors to and applications in this expanding field of research.

Utilizing surface-enhanced Raman spectroscopy [9], density functional theory [10], and digital simulation [11], Amatore and co-workers investigated the mechanism for reduction of benzyl chloride at a silver cathode in acetonitrile, particularly with respect to the existence and detection of adsorbed benzyl chloride as well as benzyl radicals and benzyl anions. Rondinini et al. [12] studied the direct reduction of haloadamantanes at silver to assess how the position of the halogen moiety affects the yield of the dimer formed via controlled-potential (bulk) electrolysis. More recently, the same laboratory has prepared silver nanoparticles and employed them as composite-supported catalysts for the reduction of chloroform to methane in an aqueous medium [13]. In other work by the group of Simonet [14,15], the behavior of alkyl iodides at silver electrodes was probed, and it was observed that homo-dimerization is the dominant process. A number of publications related to the reduction of halogenated organic compounds at silver cathodes by Isse, Gennaro, and their co-workers include investigations of the reduction of benzyl halides [16], the mechanism of dissociative electron transfer to organic chlorides [17–19], and the carboxylation of activated carbon–halogen bonds [20–22]. In our laboratory, a recent study of the reduction of an assortment of primary, secondary, and tertiary alkyl monohalides at silver cathodes was conducted [23]. In addition, electrochemical reduction (remediation) of some well-known environmentally hazardous and halogenated pollutants at silver cathodes has been examined; these compounds include freons such as CFC-113 [24–27], pesticides such as lindane [28] and DDT [29], and flame retardants such as decabromodiphenyl ether [30] and hexabromocyclododecane [31].

In the present study, we have sought to extend our knowledge of the electrochemical reduction of α,ω-dihaloalkanes by utilizing cyclic voltammetry and controlled-potential (bulk) electrolysis to investigate the direct electrochemical reductions of 1-bromo-6-chlorohexane (**1**) and 1-chloro-6-iodohexane (**2**) at silver cathodes in dimethylformamide (DMF) containing tetra-n-butylammonium tetrafluoroborate (TBABF$_4$) as the supporting electrolyte. Products resulting from bulk electrolyses of **1** and **2** have been separated, identified, and quantitated with the aid of gas chromatography (GC) and gas chromatography–mass spectrometry (GC–MS). Utilizing the information acquired, we propose mechanistic schemes for the reduction of **1** and **2**.

2. Experimental

2.1. Reagents

Each of the following chemicals was purchased and used as received unless otherwise indicated, their purities and commercial sources being given in parentheses: 1-bromo-6-chlorohexane (**1**) (95%, Sigma Aldrich), 1-chloro-6-iodohexane (**2**) (96%, Sigma Aldrich), 1,12-dichlorododecane (96+%, Acros Organics), n-hexadecane (99%, Sigma Aldrich), n-heptane (99%, Mallinckrodt), n-hexane (96%, EMD), 1-hexene (98%, Alfa Aesar), 1,5-hexadiene (98%, Sigma Aldrich), deuterium oxide (D$_2$O, 99.9 atom % D, Sigma Aldrich), and diethyl ether (absolute, anhydrous, EMD). Dimethylformamide (DMF, 99.99%, Omnisolv) was used as the solvent for all electrochemical experiments. Tetra-n-butylammonium tetrafluoroborate (TBABF$_4$, 98+%, TCI), used as the supporting electrolyte, was recrystallized from an ethyl acetate–hexane mixture, and then stored in a vacuum oven at 80 °C to exclude traces of water. Before use, 1-bromo-6-chlorohexane (**1**) was vacuum distilled. Deaeration of all solutions was accomplished with zero-grade argon (Air Products).

2.2. Electrodes, cells, and instrumentation

Cyclic voltammetry was performed in a cell previously described [32]. A silver (3.0-mm diameter, Alfa-Aesar, 99.9%) working electrode with a circular planar area of 0.071 cm^2 was used along with a coil of platinum wire which acted as the auxiliary (counter) electrode. Before each cyclic voltammogram was acquired, the working electrode was cleaned on a polishing pad (Buehler) with 0.05-μm aqueous alumina suspension and washed in an ultrasonic bath with DMF. Cyclic voltammetry experiments were performed with a Princeton Applied Research Corporation (PARC) model 2273 or 273A potentiostat that utilized a Power-Suite® software package. All data were processed with the aid of OriginPro 9 or OriginPro 2016 software.

Controlled-potential (bulk) electrolyses were performed in a two-compartment cell [33]. Silver working electrodes, each with an estimated surface area of 45 cm^2, were constructed from silver mesh (99.9%, Alfa Aesar) woven from 0.356-mm-diameter wire, with an additional single wire for the electrical lead. Prior to each electrolysis, the silver working cathodes were cleaned by ultra-sonication for at least 30 min in an aqueous sodium bicarbonate paste, then washed with distilled water and dried for 20 min in an oven at 180 °C. Owing to the volatility of products arising from reductions of **1** and **2**, sparging of argon through the cathode compartment to remove oxygen was stopped when the background current of a pre-electrolysis reached a baseline level. Then the cell was sealed with parafilm, and the desired starting material was injected and electrolyzed. A carbon rod auxiliary (counter) electrode was immersed in DMF–TBABF$_4$ in the anode compartment that was separated from the cathode compartment by a sintered-glass disk backed by a methyl cellulose plug containing solvent–electrolyte. Bulk electrolyses were conducted with the aid of a PARC model 173 potentiostat that utilized a locally written data collection LabView program; the acquired data were processed with OriginPro 9 or OriginPro 2016 software.

All potentials in this paper are given with respect to a reference electrode consisting of a cadmium-saturated mercury amalgam in contact with DMF saturated with both sodium chloride and cadmium chloride; this electrode has a potential of −0.76 V versus the aqueous saturated calomel electrode (SCE) at 25 °C [34–36].

2.3. Separation, identification, and quantitation of products

All product identification was accomplished with the aid of gas chromatography–mass spectrometry (GC–MS); an Agilent 6890N gas chromatograph, fitted with a 30 m × 0.25 mm capillary column with a 0.25 μm DB-5 stationary phase consisting of 5% phenyl-polysiloxane and 95% methylpolysiloxane (J & W Scientific), was used in tandem with an Agilent 5973 inert mass-selective detector operating in electron ionization mode (70 eV). Deuterium
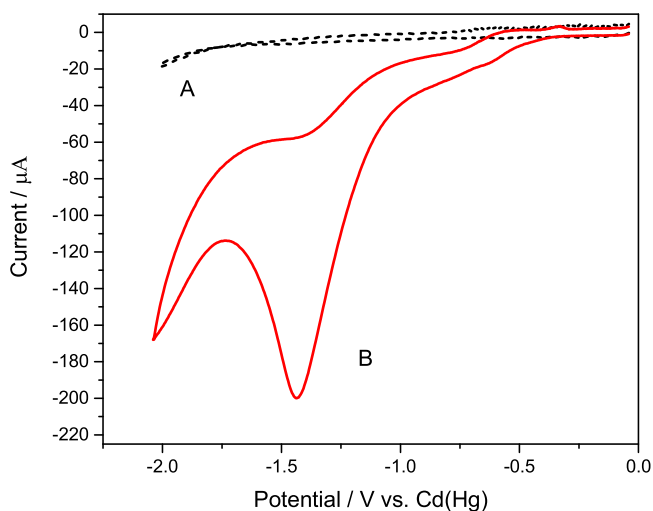
incorporation was measured with a Thermo MAT-95 XP magnetic sector mass spectrometer with a Thermo Trace GC as an inlet under conditions similar to those described above for the Agilent system; the degree of isotopic incorporation was computed as described elsewhere [37].

Before each bulk electrolysis, known amounts of internal standards (*n*-heptane and *n*-hexadecane) were injected into the catholyte. At the end of each experiment, the catholyte was partitioned between cold water and diethyl ether; the resulting organic layer was washed twice with cold water, dried over anhydrous sodium sulfate, and concentrated via rotary evaporation. Products were separated and quantitated by use of an Agilent 7890A gas chromatograph, equipped with a flame-ionization detector; 1,12-dichlorododecane, 1-chlorohexane, and 6-chloro-1-hexene were separated with the DB-5 column described above, whereas more volatile products (1,5-hexadiene, 1-hexene, and *n*-hexane) required separation by a 12.5-m (including a 2.5-m particle trap) × 0.53-mm × 20-μm PLOT fused-silica capillary column (Varian). Using a procedure described in earlier research [38], we determined the product distributions in this report from gas chromatographic response factors and peak areas measured with the aid of Agilent ChemStation software.
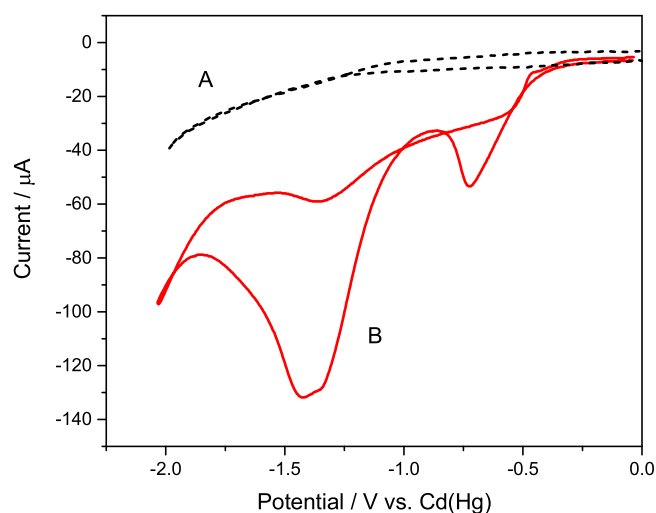
3. Results and discussion

3.1. Cyclic voltammetric behavior of 1-bromo-6-chlorohexane (**1**) and 1-chloro-6-iodohexane (**2**)

Fig. 1 depicts a cyclic voltammogram recorded at $100\,\text{mV s}^{-1}$ for the reduction of a 5.0 mM solution of 1-bromo-6-chlorohexane (**1**) at a silver electrode in DMF containing 0.050 M TBABF$_4$. One major irreversible cathodic peak is observed at $-1.45\,\text{V}$, and there is a small (possibly reversible) peak on the rising portion of the large peak. Shown in Fig. 2 is a cyclic voltammogram recorded at $100\,\text{mV s}^{-1}$ for the reduction of a 5.0 mM solution of 1-chloro-6-iodohexane (**2**) at a silver electrode in DMF containing 0.050 M TBABF$_4$. Two irreversible peaks are seen at -0.63 and $-1.36\,\text{V}$, the second of which is clearly dominant and which, for some recorded cyclic voltammograms, appears as two closely overlapped peaks. In fact, we spent significant time recording many cyclic
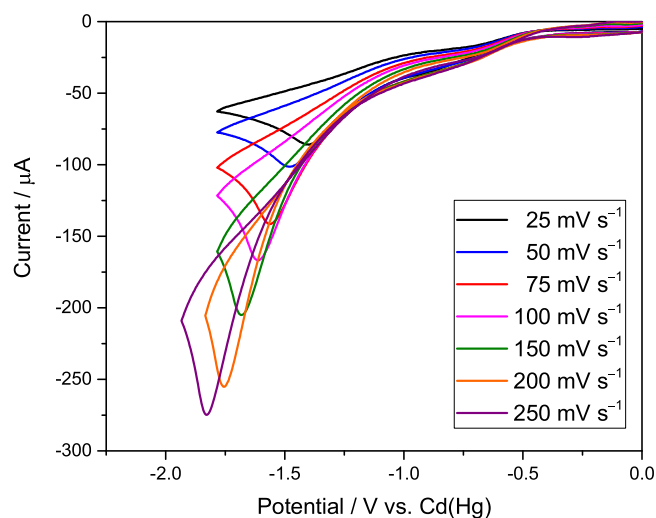

Fig. 2. Cyclic voltammograms recorded with a silver electrode (geometric area = 0.071 cm^2) at 100 mV s^{-1} in oxygen-free DMF containing 0.050 M TBABF$_4$ (curve A) and 5.0 mM 1-chloro-6-iodohexane, **2** (curve B). Scans go from ca. 0 to -2.2 to 0 V. Potentials are given with respect to a cadmium-saturated mercury amalgam reference electrode in contact with DMF saturated with both cadmium chloride and sodium chloride; this electrode has a potential of -0.76 V versus SCE at 25 °C.

voltammograms for this compound with the same electrode and with different electrodes; the cyclic voltammogram shown in Fig. 2 is the most "representative" of what we typically observed. Unfortunately, we do not yet have an explanation for this phenomenon. For example, the appearance or absence of a "double" peak does not seem related in any obvious way to the polishing procedure done between scans. Moreover, for bulk electrolyses of **2** discussed in the next section of this paper, the potential was always set at a value (-1.60 V) to be significantly more negative than the second (single or double) major peak.

In addition, we recorded cyclic voltammograms for reduction of both **1** and **2** at scan rates ranging from 25 to 250 mV s^{-1}, as shown in Figs. 3 and 4, respectively. For each of the predominant second cathodic peaks for reduction of **1** and **2**, we found that I_{pc} increases
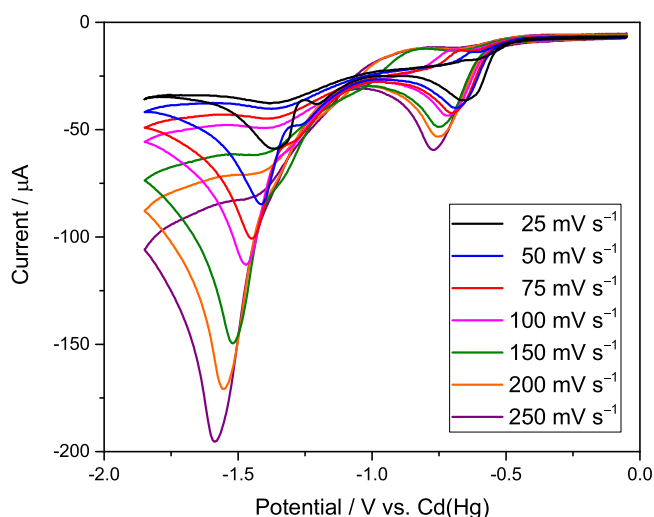

Fig. 1. Cyclic voltammograms recorded with a silver electrode (geometric area = 0.071 cm^2) at 100 mV s^{-1} in oxygen-free DMF containing 0.050 M TBABF$_4$ (curve A) and 5.0 mM 1-bromo-6-chlorohexane, **1** (curve B). Scans go from ca. 0 to -2.2 to 0 V. Potentials are given with respect to a cadmium-saturated mercury amalgam reference electrode in contact with DMF saturated with both cadmium chloride and sodium chloride; this electrode has a potential of -0.76 V versus SCE at 25 °C.

Fig. 3. Cyclic voltammograms recorded at scan rates of 25, 50, 75, 100, 150, 200, and 250 mV s^{-1} for reduction of 5.0 mM 1-bromo-6-chlorohexane (**1**) at a silver cathode (area = 0.071 cm^2) in oxygen-free DMF containing 0.050 M TBABF$_4$. Scans go from ca. 0 to -2.0 to 0 V. Potentials are given with respect to a cadmium-saturated mercury amalgam reference electrode in contact with DMF saturated with both cadmium chloride and sodium chloride; this electrode has a potential of -0.76 V versus SCE at 25 °C.

Fig. 4. Cyclic voltammograms recorded at scan rates of 25, 50, 75, 100, 150, 200, and 250 mV s^{-1} for reduction of 5.0 mM 1-chloro-6-iodohexane (**2**) at a silver cathode (area = 0.071 cm^2) in oxygen-free DMF containing 0.050 M TBABF$_4$. Scans go from ca. −0.07 to −1.85 to −0.07 V. Potentials are given with respect to a cadmium-saturated mercury amalgam reference electrode in contact with DMF saturated with both cadmium chloride and sodium chloride; this electrode has a potential of −0.76 V versus SCE at 25 °C.

in proportion to $v^{1/2}$. On the other hand, the first peak for reduction of **2** is proportional to v between 25 and 250 mV s^{-1}; it is noteworthy that this first peak is symmetrical in shape, which may be indicative of species adsorption onto the surface of the silver cathode. For the specified range of scan rates, E_{pc} shifted (by various increments) to more negative values: (a) for **1**, E_{pc} shifted from −1.41 to −1.82 V (a change of 410 mV); (b) for **2**, E_{pc} for the first peak shifted from −0.65 to −0.77 V (a change of 120 mV) and E_{pc} for the second peak shifted from −1.36 to −1.59 V (a change of 230 mV). Thus, in all cases, the value of $\Delta E_{p}/\Delta\log(v)$ greatly exceeded the diagnostic (−59.2 mV per log unit) which would be expected for a stepwise mechanism where the initial electron transfer is the rate-determining step (with a transfer coefficient, α, close to 0.5) [39]. However, using the equation $\alpha = -1.15(RT/F)$ ($\Delta\log v/\Delta E_{pc}$), we calculated transfer coefficients lower than 0.5 that ranged from 0.07 to 0.24. These small transfer coefficients are indicative of the large driving force required to cleave carbon–halogen bonds and are consistent with a concerted mechanism [39]. This finding is in accord with previous reports which indicate that reduction of aliphatic halides at silver cathodes occurs via a concerted electron-transfer mechanism. Isse and coworkers [40] comment that the absence of an energetically accessible π* orbital and the high energy of the σ* carbon–halogen

orbital makes the formation of a radical–anion unfavorable; the incoming electron must move into an elongated carbon–halogen bond, which is cleaved upon injection of the electron, resulting in a concerted process.

3.2. Controlled-potential (bulk) electrolyses of 1-bromo-6-chlorohexane (1) and 1-chloro-6-iodohexane (2)

Summarized in Table 1 are coulometric data and product distributions arising from bulk electrolyses of **1** and **2** at silver gauze electrodes in DMF containing 0.050 M TBABF$_4$ with applied potentials chosen to correspond to the major cathodic peaks revealed by cyclic voltammetry (Figs. 1 and 2). Each entry corresponds to the average of at least three reproducible experiments. Percentages represent the amount of starting material converted into each product.

Reduction of **1** results in a coulometric n value of 1.4, indicating the likely generation of carbanion intermediates; 1-chlorohexane (**3**) was the major product, along with 6-chloro-1-hexene (**4**), 1,5-hexadiene (**5**), 1-hexene (**6**), and n-hexane (**7**). Increasing the concentration of **1** had little effect on the product distribution (Table 1, entry 2), except that the yields of **3** and **4** were increased and decreased, respectively. Because the potential for complete reduction of 1-chlorohexane is more negative than the potential used to reduce **1**, we are not surprised to find 1-chlorohexane as the major product. When **1** was electrolyzed at −1.60 V in the presence of a 100-fold excess of D$_2$O, we found that the resulting 1-chlorohexane was monodeuterated to an extent of 52%, an observation that supports the intermediacy of carbanions.

A reviewer of the first version of our manuscript raised an interesting question concerning whether bromide ion, arising from the reduction of **1**, might be adsorbed onto the silver cathode such that the reduction of **1** is affected. One piece of evidence against this proposal is that no unreduced **1** remained at the end of bulk electrolyses conducted at −1.60 V (Table 1, entries 1 and 2). Even more compelling information is provided in a publication by Falciola and coworkers [41] which indicates that, at potentials more negative than −1.4 V vs. SCE (or −0.64 V vs. our reference electrode), bromide ion is desorbed completely from silver. Therefore, for the reduction of **1**, we believe that adsorption–desorption of bromide ion does not play a significant role. An analogous situation was encountered in an earlier study [31] from our laboratory of the reduction of 1,2,5,6,9,10-hexabromocyclodo-decane at silver in dimethylformamide containing 0.10 M tetra-methylammonium tetrafluoroborate.

Electrolyses of **2** at a potential of −0.95 V (corresponding to the first voltammetric peak) resulted in an n value of 1.1, an observation indicating the dominance of radical intermediates. Major products were 1-chlorohexane (**3**), 6-chloro-1-hexene (**4**),

Table 1
Coulometric n values and product distributions for electrochemical reduction of 1-bromo-6-chlorohexane (**1**) and 1-chloro-6-iodohexane (**2**) at silver mesh cathodes in oxygen-free DMF containing 0.050 M TBABF$_4$.

Entry	Substrate	Concentration (mM)	E (V)	n[a]	Product distribution (%)[b]						
					3	**4**	**5**	**6**	**7**	**8**	Total
1	**1**	5.0	−1.60	1.4	48	21	4	7	19	ND[c]	99
2	**1**	10.0	−1.60	1.4	63	10	4	5	18	ND[c]	100
3	**2**	5.0	−0.95	1.1	27	22	TR[d]	TR[d]	ND[c]	33	82
4	**2**	10.0	−0.95	1.1	34	19	TR[d]	TR[d]	ND[c]	40	93
5	**2**	5.0	−1.60	1.3	52	21	3	5	5	8	94
6	**2**	10.0	−1.60	1.1	43	23	2	1	5	22	96

3 = 1-chlorohexane; **4** = 6-chloro-1-hexene; **5** = 1,5-hexadiene; **6** = 1-hexene; **7** = n-hexane; **8** = 1,12-dichlorododecane.
[a] Average number of electrons per molecule of **1** or **2**.
[b] Yield expressed as the percentage of **1** or **2**.
[c] ND = not detected.
[d] TR = trace.

and 1,12-dichlorododecane (**8**). As anticipated, doubling the concentration of **2** resulted in an increase in the production of the dimer (**8**). In addition, we observed small amounts of completely dehalogenated products [1,5-hexadiene (**5**) and 1-hexene (**6**)]. Reduction of **2** at a potential of −1.60 V (corresponding to the second voltammetric peak) resulted in an *n* value of 1.3, suggesting a mixture of one- and two-electron processes. Addition of D_2O for the reduction of **2** at −0.95 V resulted in no incorporation of deuterium into the resulting 1-chlorohexane (**3**); however, we did find that 1-chlorohexane (**3**) was mono-deuterated to an extent of 56% when **2** was reduced at a potential of −1.60 V in the presence of a 100-fold excess of D_2O. These results support the conclusion that the reduction of **2** at −0.95 V occurs via a radical mechanism, whereas the electrolysis of **2** at −1.6 V proceeds through a mixture of one- and two-electron transfers. Reduction at the more negative potential generated the same set of products, but with a different distribution. When the concentration of **2** was 5 mM, a dramatic decrease in dimer formation occurred, allowing the production of 1-chlorohexane to increase. At a higher concentration (10 mM) of **2**, formation of the dimer increases and the *n* value decreases correspondingly, which indicates the predominance of radical processes and enhanced radical coupling.

3.3. Mechanistic aspects of the reduction of 1-bromo-6-chlorohexane (**1**)

Depicted in Scheme 1 is a suggested set of mechanistic steps for the reduction of **1**. In the first reaction, **1** accepts a pair of electrons, resulting in loss of a bromide ion, to give **9**, which can be subsequently protonated by residual water in the solvent–electrolyte to give 1-chlorohexane (**3**). It is definitely conceivable that the overall two-electron process occurs in a stepwise fashion to produce a transient radical intermediate that is immediately reduced to a carbanion via uptake of a second electron to afford **9**. In reaction 2, carbanion **9** (acting as a base) deprotonates a molecule of the starting material (**1**), leading to expulsion of a bromide ion and formation of 6-chloro-1-hexene (**4**). Alternatively, as shown in reaction 3, **1** and **9** can interact to afford 6-bromo-1-hexene (**10**) as well as **3** and a chloride ion. As depicted in reaction 4, **10** can undergo a classic two-electron cleavage of its carbon–bromine bond (with protonation by residual water) to produce 1-hexene (**6**). In reaction 5, we show that either **4** or **10** can
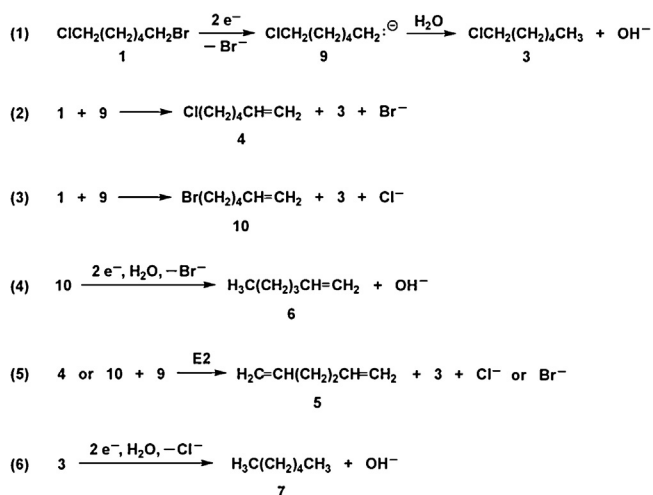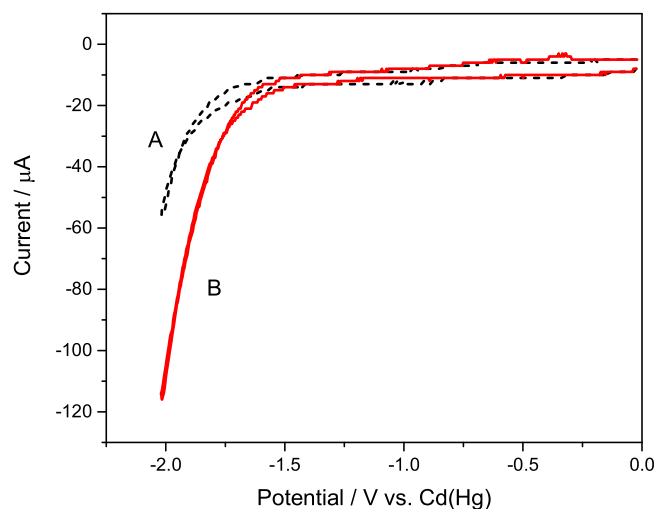
Fig. 5. Cyclic voltammograms recorded with a silver electrode (geometric area = 0.071 cm^2) at 100 mV s^{-1} in oxygen-free DMF containing 0.050 M TBABF$_4$. Curve A: no added 1-chlorohexane; curve B: with 5.0 mM 1-chlorohexane. Scans go from ca. 0 to −2.0 to 0 V. Potentials are given with respect to a cadmium-saturated mercury amalgam reference electrode in contact with DMF saturated with both cadmium chloride and sodium chloride; this electrode has a potential of −0.76 V versus SCE at 25 °C.

be deprotonated by **9** to eliminate a chloride or bromide ion, respectively, and to yield **3**. Finally, as shown in reaction 6, **3** can be reductively dechlorinated to give *n*-hexane (**7**). To confirm the occurrence of this last process, we carried out additional cyclic voltammetry and bulk electrolysis experiments. Fig. 5 shows a comparison between cyclic voltammograms for the solvent–supporting electrolyte alone (curve A) and solvent–supporting electrolyte containing 5.0 mM 1-chlorohexane (curve B). Although no obvious voltammetric peak is seen in curve B, it is nevertheless evident that some reduction of 1-chlorohexane does occur at −1.60 V. Indeed when we electrolyzed a solution containing 5.0 mM 1-chlorohexane in DMF–TBABF$_4$ at a potential of −1.60 V, subsequent gas chromatographic analysis revealed the presence of *n*-hexane. Therefore, we conclude that, on the time scale of a bulk electrolysis of **1**, production of *n*-hexane can occur, as evidenced by the product distributions compiled in Table 1.

A final mechanistic point pertains to the roles played by OH$^-$ and **9** as bases in Scheme 1. As seen in reactions 1, 4, and 6, OH$^-$ arises via protonation of electrogenerated alkyl carbanions by residual water that is present in the solvent–supporting electrolyte; typically, the concentration of this adventitious water is approximately 40 mM [42]. On the basis of the roster of products observed for the reduction of **1**, we conclude that OH$^-$ is not a viable base in terms of its S$_N$2 attack on carbon–halogen bonds, because no alcohols were detected as products. In two earlier papers [42,43] from our laboratory, hydroxide ions arising from the protonation by residual water of *n*-decyl carbanions arising from the reductive cleavage of 1-iododecane did afford 1-decanol, the production of which was ascribed to attack of OH$^-$ on yet unreduced alkyl iodide. However, in the present work, we regard **9** as a much more potent base than OH$^-$ for the deprotonation of **1**, **4**, and **10** (as shown for reactions 2, 3, and 5 in Scheme 1) that leads to the formation of olefins.

3.4. Mechanistic aspects of the reduction 1-chloro-6-iodohexane (**2**)

Scheme 2 provides a suggested sequence of mechanistic steps for the reduction of **2**; reactions 1 through 4 involve radical intermediates that arise from one-electron reduction of **2** at

(1) $\quad$ ClCH$_2$(CH$_2$)$_4$CH$_2$Br $\xrightarrow[\text{− Br}^-]{\text{2 e}^-}$ ClCH$_2$(CH$_2$)$_4$CH$_2$:$^\ominus$ $\xrightarrow{\text{H}_2\text{O}}$ ClCH$_2$(CH$_2$)$_4$CH$_3$ + OH$^-$
$\qquad\qquad$ **1** $\qquad\qquad\qquad\qquad\qquad\qquad$ **9** $\qquad\qquad\qquad\qquad\qquad$ **3**

(2) $\quad$ **1** + **9** $\longrightarrow$ Cl(CH$_2$)$_4$CH=CH$_2$ + **3** + Br$^-$
$\qquad\qquad\qquad\qquad\qquad$ **4**

(3) $\quad$ **1** + **9** $\longrightarrow$ Br(CH$_2$)$_4$CH=CH$_2$ + **3** + Cl$^-$
$\qquad\qquad\qquad\qquad\qquad$ **10**

(4) $\quad$ **10** $\xrightarrow{\text{2 e}^-, \text{H}_2\text{O}, -\text{Br}^-}$ H$_3$C(CH$_2$)$_3$CH=CH$_2$ + OH$^-$
$\qquad\qquad\qquad\qquad\qquad\qquad$ **6**

(5) $\quad$ **4** or **10** + **9** $\xrightarrow{\text{E2}}$ H$_2$C=CH(CH$_2$)$_2$CH=CH$_2$ + **3** + Cl$^-$ or Br$^-$
$\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ **5**

(6) $\quad$ **3** $\xrightarrow{\text{2 e}^-, \text{H}_2\text{O}, -\text{Cl}^-}$ H$_3$C(CH$_2$)$_4$CH$_3$ + OH$^-$
$\qquad\qquad\qquad\qquad\qquad\qquad$ **7**

Scheme 1. Proposed mechanistic steps involved in the reduction of 1-bromo-6-chlorohexane (**1**) at silver cathodes in dimethylformamide (DMF) containing 0.050 M TBABF$_4$.
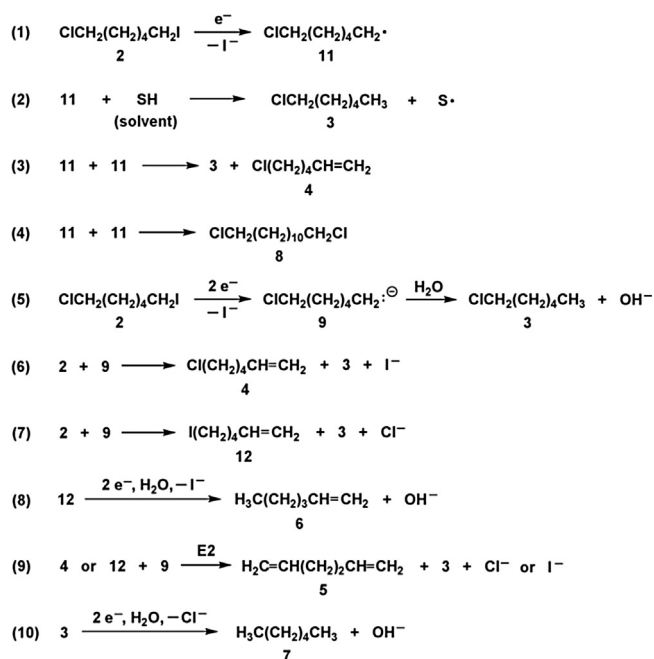
(1) $ClCH_2(CH_2)_4CH_2I \xrightarrow[-I^-]{e^-} ClCH_2(CH_2)_4CH_2\cdot$
   2   **11**

(2) $11 + SH \longrightarrow ClCH_2(CH_2)_4CH_3 + S\cdot$
    (solvent)   **3**

(3) $11 + 11 \longrightarrow 3 + Cl(CH_2)_4CH=CH_2$
           4

(4) $11 + 11 \longrightarrow ClCH_2(CH_2)_{10}CH_2Cl$
           8

(5) $ClCH_2(CH_2)_4CH_2I \xrightarrow[-I^-]{2e^-} ClCH_2(CH_2)_4CH_2{:}^{\ominus} \xrightarrow{H_2O} ClCH_2(CH_2)_4CH_3 + OH^-$
   2   **9**   **3**

(6) $2 + 9 \longrightarrow Cl(CH_2)_4CH=CH_2 + 3 + I^-$
        4

(7) $2 + 9 \longrightarrow I(CH_2)_4CH=CH_2 + 3 + Cl^-$
        12

(8) $12 \xrightarrow{2e^-, H_2O, -I^-} H_3C(CH_2)_3CH=CH_2 + OH^-$
          6

(9) $4 \text{ or } 12 + 9 \xrightarrow{E2} H_2C=CH(CH_2)_2CH=CH_2 + 3 + Cl^- \text{ or } I^-$
           5

(10) $3 \xrightarrow{2e^-, H_2O, -Cl^-} H_3C(CH_2)_4CH_3 + OH^-$
         7

Scheme 2. Proposed mechanistic steps involved in the reduction of 1-chloro-6-iodohexane (**2**) at silver cathodes in dimethylformamide (DMF) containing 0.050 M TBABF$_4$.

−0.95 V, whereas carbanion intermediates formed via two-electron reduction of **2** at −1.60 V appear in reactions 5 through 10.

In reaction 1, we propose that **2** accepts a single electron, resulting in the loss of an iodide ion to give a 6-chlorohex-1-yl radical (**11**). Once formed, **11** can engage is three different processes: (a) abstraction of a hydrogen atom from the solvent to form **3** (reaction 2); (b) radical disproportionation to afford **3** and **4** (reaction 3); and (c) radical coupling to yield **8** (reaction 4).

As a starting point for the reduction of **2** at −1.60 V, reaction 5 involves two-electron cleavage of its carbon–iodine bond to form **9**, which is protonated by residual water in the solvent–electrolyte to give **3**. In reaction 6, **2** and **9** interact to yield **3** and **4** along with an iodide ion. Alternatively, reaction 7 shows that interaction between **2** and **9** can lead to the formation of **3** and **12** together with a chloride ion. In reaction 8, **12** undergoes a conventional two-electron reduction that leads to **6**. Reaction 9 depicts base-catalyzed E2 elimination reactions that produce **5** and **3**, and reaction 10 is another classic two-electron reduction of **3** to afford **7**. With respect to the formation of 1,12-dichlorododecane via reduction of **2** at −1.60 V (Table 1, entries 5 and 6), we prefer a process (Scheme 2, reaction 4) that involves coupling of 6-chlorohex-1-yl radicals (**11**), especially because coulometric n values for reduction of **2** indicate that a mixture of one- and two-electron events does take place.

4. Conclusions and future research

Cyclic voltammetry and controlled-potential (bulk) electrolysis have been employed to investigate the direct electrochemical reductions of 1-bromo-6-chlorohexane (**1**) and 1-chloro-6-iodo-hexane (**2**) at silver cathodes in dimethylformamide (DMF) containing 0.050 M tetra-n-butylammonium tetrafluoroborate (TBABF$_4$). A cyclic voltammogram for the reduction of **1** displays one major irreversible cathodic peak, whereas two irreversible cathodic peaks are seen in a cyclic voltammogram for reduction of **2**. Major products arising from bulk electrolyses of **1** at −1.60 V were found to be 1-chlorohexane, 6-chloro-1-hexene, and n-hexane. On the other hand, electrochemical reduction of **2** at either

−0.95 or −1.60 V affords mainly 1-chlorohexane, 6-chloro-1-hexene, and 1,12-dichlorododecane, along with traces of 1,5-hexadiene and 1-hexene, whereas reduction of **2** at −1.60 V forms 1,12-dichlorododecane in substantial yield. Electrolyses of **2** at −0.95 V (first cathodic peak) in the presence of excess D$_2$O led to no incorporation of deuterium, which indicates the absence of carbanion intermediates. However, when both **1** and **2** were electrolyzed at −1.60 V in the presence of excess D$_2$O, there was approximately 50% incorporation of deuterium into 1-chlorohexane, which is evidence for a carbanion intermediate.

Another matter for brief mention here is the possibility or likelihood that one or both of the parent compounds (as well as electrogenerated intermediates) undergo adsorption onto a silver cathode. In the course of preliminary research [44] in our laboratory, early evidence [(a) electrochemical surface-enhanced Raman spectroscopy (EC–SERS), (b) calculations based on the use of density functional theory (DFT), and (c) surface interrogation mode of scanning electrochemical microscopy (SI–SECM)] has offered enticing results pertaining to possible adsorption of 1-bromodecane and 1-iododecane (and perhaps intermediates arising from their reduction) onto silver cathodes. At a future time, we hope to report results from this work and to extend these efforts to the reduction of other halogenated compounds at silver electrodes.

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