Electrochemical Reduction of 1,6-Dihalohexanes at Carbon Cathodes in Dimethylformamide

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Cyclic voltammograms for the reduction of 1,6-dibromo-, 1,6-diiodo-, 1-bromo-6-chloro-, and 1-chloro-6-iodohexane at glassy carbon electrodes in dimethylformamide containing tetramethylammonium perchlorate exhibit single irreversible waves that correspond to the reductive cleavage of carbon–bromine or carbon–iodine bonds. When large-scale controlled-potential electrolyses of either 1,6-dibromo- or 1,6-diiodohexane are performed at reticulated vitreous carbon, the principal products are *n*-hexane (30–45%), 1-hexene (28–34%), 1,5-hexadiene (6–16%), and cyclohexane (<7%), with *n*-dodecane being another significant species obtained from 1,6-diiodohexane. Because a carbon–chlorine bond is not directly reducible, 1-bromo-6-chloro- and 1-chloro-5-iodohexane give rise mainly to 1-chlorohexane (47–64%), 6-chloro-1-hexene (20–33%), and 1,12-dichlorododecane (2–25%). From these product distributions, and with the aid of experiments done in the presence of deuterium-labeled reagents, we conclude that the electrolytic reduction of 1,6-diiodo- and 1-chloro-6-iodohexane involves both radical and carbanion intermediates, whereas only carbanionic pathways are important for electrolyses of 1,6-dibromo- and 1-bromo-6-chlorohexane.

As part of a continuing investigation of the electrochemical reduction of alkyl halides in our laboratory, the behavior of several families of α,ω-dihaloalkanes at carbon cathodes in dimethylformamide has been examined. In a study of the electrochemistry of five different 1,3-dihalopropanes,[1] we observed that these compounds undergo two-electron reduction to give a 3-haloprop-1-yl carbanion which cyclizes intramolecularly to afford cyclopropane in high yield (>86%). In parallel work dealing with the reduction of a number of 1,4-dihalobutanes[2] and 1,5-dihalopentanes,[3] it was found that substantial quantities of cyclobutane and cyclopentane arise, respectively, from the electrogenerated 4-halobut-1-yl and 5-halopent-1-yl carbanions; in addition, depending on the identity of the α,ω-dihaloalkane, on the choice of potential, and on the presence or absence of proton donors, other acyclic products including *n*-butane, 1-butene, *cis*- and *trans*-2-butene, 1-halobutane, *n*-octane, 1-halooctane, and 1,8-dihalooctane are derived from the 1,4-dihalobutanes, whereas *n*-pentane, 1-pentene, *cis*- and *trans*-2-pentene, 1-halopentane, *n*-decane, 1,10-dihalodecane, 1-decene, *n*-pentadecane, and 1-pentadecene are among the compounds formed from the electrochemical reduction of 1,5-dihalopentanes. Thus, it is clear that the electrolysis of 1,4-dihalobutanes and 1,5-dihalopentanes can involve both radical and carbanion intermediates.

In this paper we report the results of an investigation of the direct electrochemical reduction of 1,6-dibromo-, 1,6-diiodo-, 1-bromo-6-chloro-, and 1-chloro-6-iodohexane at carbon electrodes in dimethylformamide containing tetramethylammonium perchlorate. No previous work pertaining to the electrochemical behavior of these compounds at carbon cathodes has been described in the literature. We have used cyclic voltammetry, controlled-potential electrolysis, and deuterium-labeled trapping agents to establish that radical and carbanion intermediates are both involved in the product-forming pathways.

Experimental Section

Reagents. Dimethylformamide (DMF), employed as solvent throughout this work, was Burdick & Jackson "distilled in glass" material and was used without further purification. Tetramethylammonium perchlorate (TMAP) obtained from GFS Chemicals, Inc., was used as supporting electrolyte and was stored in a desiccator over Drierite. All deaeration procedures were carried out with Air Products UHP-grade argon.

Each of the following reagents was used as received: 1,6-dibromohexane (Aldrich, 97%), 1,6-diiodohexane (Aldrich, 97%), 1-bromo-6-chlorohexane (Aldrich, 97%), 1-chloro-6-iodohexane (Lancaster, 97%), *n*-hexane (Aldrich, 99+%), 1-hexene (Aldrich, 97%), 1,5-hexadiene (Aldrich, 98%), cyclohexane (Fisher, 99%), *n*-dodecane (Aldrich, 99%), 1-dodecene (Aldrich, 95%), *n*-octadecane (Aldrich, 99%), 1-octadecene (Aldrich, 90%), 1-chlorohexane (Aldrich, 99%), 1,12-dichlorododecane (Pfaltz & Bauer, 98%), heptyl cyanide (Aldrich, 97%), diethyl malonate-d_2 (Aldrich, 90 atom % D), 1,1,1,3,3,3-hexafluoro-2-propanol (Aldrich, 99+%), *n*-octane (Aldrich, 99+%), 1-hexanol (Matheson, Coleman and Bell, 98%), 5-hexen-1-ol (Aldrich, 99%), deuterium oxide (Cambridge Isotope Laboratories, 99.83 atom % D), and acetonitrile-d_3 (Aldrich, 99.5 atom % D).

Preparation of Diethyl *n*-Hexylmalonate. To a stirred solution of sodium (2.3 g, 0.10 mol) in 50 mL of absolute ethanol, was added diethyl malonate (18.1 mL, 0.12 mol) followed by 1-bromohexane (14 mL, 0.10 mol). After being stirred for 30 min, the mixture was extracted with diethyl ether, and the ether phase was washed twice with water, dried over magnesium sulfate, and concentrated. Finally, the desired product was obtained by means of vacuum distillation (bp 147–150 °C, 10 Torr); mass spectrum (70 eV) *m/z* 199, $[M - OC_2H_5]^+$ (24%); 173, $[M - C_5H_{11}]^+$ (27%); 160, $[M - C_6H_{12}]^+$ (100%), which is similar to that seen in our earlier research[4,5] for diethyl *n*-decylmalonate.

Cells, Electrodes, Instrumentation, and Procedures. Cells, instrumentation, and procedures for cyclic voltammetry

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and controlled-potential electrolysis are described elsewhere.[6,7] For cyclic voltammetry, a 3-mm-diameter glassy carbon rod (Grade GC-20, Tokai Electrode Manufacturing Co., Tokyo, Japan) was press-fitted into Teflon to give a planar, circular working electrode with a geometric area of 0.077 cm^2. For controlled-potential electrolyses, we used reticulated vitreous carbon discs with surface areas of approximately 200 cm^2; procedures for fabrication, cleaning, and handling of these electrodes are presented in a previous paper.[4] All potentials are quoted with respect to a reference electrode consisting of a saturated cadmium amalgam in contact with DMF saturated with both cadmium chloride and sodium chloride; this electrode has a potential of −0.76 V vs the aqueous saturated calomel electrode at 25 °C.[8,9]

Procedures and equipment for the separation, identification, and quantitation of the electrolysis products by means of both gas chromatography and GC-MS are described in earlier publications.[6,10] To quantitate the products, we employed *n*-octane as an electroinactive internal standard, which was added to each solution prior to the start of an electrolysis. All product yields reported in this paper are absolute and represent the percentage of starting material incorporated into a particular species.

Product Identification. We identified *n*-hexane, 1-hexene, 1,5-hexadiene, cyclohexane, *n*-dodecane, 1-dodecene, *n*-octadecane, 1-octadecene, 1-hexanol, 5-hexen-1-ol, 1-chlorohexane, and 1,12-dichlorododecane by comparing the gas chromatographic retention times of the suspected products with those of commercially available authentic samples.

Diethyl *n*-hexylmalonate-*d*, observed to have a gas chromatographic retention time virtually equal to that of its undeuteriated analogue, was identified with the aid of GC-MS. Its mass spectrum was identical with that of diethyl *n*-hexylmalonate given above, except for the appearance of additional characteristic signals corresponding to the molecular ion with *m/z* 245 (1%) and to a fragment with *m/z* 200, $[M - OC_2H_5]^+$ (15%).

Another product, 1,1-dideuterioheptyl cyanide, with a gas chromatographic retention time the same as that for the undeuteriated commercial reagent, was distinguished from the latter compound by means of mass spectrometry; *m/z* (70 eV) 127, M^+ (2%); 126, $[M - H]^+$ (2%); 112, $[M - CH_3]^+$ (14%); 99, $[M - C_2H_4]^+$ (24%); 98, $[M - C_2H_5]^+$ (44%); 85, $[M - C_3H_6]^+$ (49%); 84, $[M - C_3H_7]^+$ (100%); 71, $[M - C_4H_8]^+$ (31%); 57, $[M - C_5H_{10}]^+$ (25%).

Four other electrolysis products were identified with the aid of mass spectral data at 70 eV: (a) for 7-cyano-7,7-dideuterio-1-heptene, *m/z* 125, M^+ (2%); 124, $[M - H]^+$ (17%); 97, $[M - C_2H_4]^+$ (16%); 96, $[M - C_2H_5]^+$ (25%); 95, $[M - C_2H_6]^+$ (51%); 84, $[M - C_3H_5]^+$ (29%); 57, $[M - C_5H_8]^+$ (29%); 55, $[M - C_2H_4CD_2CN]^+$ (100%); (b) for 7-chloro-1-cyano-1,1-dideuterioheptane, *m/z* 162, $[M - H]^+$ (0.3%); 160, $[M - H]^+$ (0.9%); 126, $[M - Cl]^+$ (57%); 99, $[M - C_2H_3Cl]^+$ (34%); 98, $[M - C_2H_4Cl]^+$ (57%); 85, $[M - C_3H_5Cl]^+$ (52%); 84, $[M - C_3H_6Cl]^+$ (83%); 56, $[M - C_5H_{10}Cl]^+$ (22%); 55, $[M - C_5H_{11}Cl]^+$ (100%); (c) for diethyl (6-chlorohexyl)malonate-*d*, *m/z* 281, M^+ (0.2%); 279, M^+ (0.3%); 236, $[M - OC_2H_5]^+$ (6%); 234, $[M - OC_2H_5]^+$ (17%); 173, $[M - C_5H_{11}Cl]^+$ (26%); 161, $[M - C_6H_{11}Cl]^+$ (69%); 160, $[M - C_6H_{12}Cl]^+$ (100%); (d) for 6-chloro-1-hexene, *m/z* 120, M^+ (3%); 118, M^+ (8%); 92, $[M - C_2H_4]^+$ (6%); 90, $[M - C_2H_4]^+$ (17%); 82, $[M - HCl]^+$ (31%); 69, $[M - CH_2Cl]^+$ (49%); 55, $[M - C_2H_4Cl]^+$ (100%).

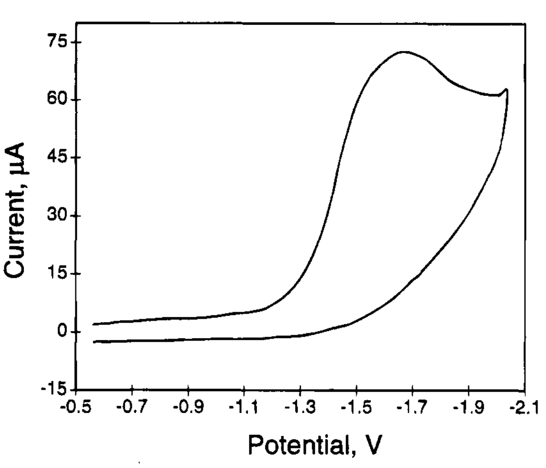

Figure 1. Cyclic voltammogram recorded at 100 mV s^{-1} for reduction of a 2 mM solution of 1,6-dibromohexane in DMF containing 0.10 M TMAP at a glassy carbon cathode (area = 0.077 cm^2).

Results and Discussion

Cyclic Voltammetric Behavior of 1,6-Dihalohexanes. As shown in Figure 1, when a cyclic voltammogram is recorded at 100 mV s^{-1} for reduction of a 2 mM solution of 1,6-dibromohexane at a glassy carbon electrode in DMF containing 0.10 M TMAP, one irreversible wave with a peak potential of −1.65 V is observed. For the same conditions used to obtain the cyclic voltammogram in Figure 1, reduction of the other 1,6-dihalohexanes that were investigated gives a single irreversible voltammetric wave with the following peak potentials: 1,6-diiodohexane, −1.38 V; 1-bromo-6-chlorohexane, −1.60 V; and 1-chloro-6-iodohexane, −1.30 V.

In a recently completed investigation,[11] we determined that the cyclic voltammetric peak potentials for 1-bromo-4-chlorobutane and 1-bromo-5-chloropentane were both −1.60 V and that those for 1-chloro-4-iodobutane and 1-chloro-5-iodopentane were both −1.31 V. Although these results agree exceedingly well with the values reported above for the homologous 1-bromo-6-chloro- and 1-chloro-6-iodohexane, these findings differ somewhat from those obtained in earlier research[2,3] conducted in our laboratory. Unfortunately, a problem that plagues the reproducibility of peak potentials measured by different workers with glassy carbon cathodes is the difficulty associated with the pretreatment and cleanliness of solid electrode surfaces. A review[12] and a recent paper[13] provide discussions and references concerning these problems as well as the numerous methods used for the preparation and activation of carbon electrodes.

Controlled-Potential Electrolyses of 1,6-Dihalohexanes. Listed in Tables 1−4 are coulometric data and product distributions obtained from controlled-potential electrolyses of the four 1,6-dihalohexanes at reticulated vitreous carbon cathodes in DMF containing 0.10 M TMAP. Each entry corresponds to the average of two or three separate experiments. What is significant about the product distributions for electrolyses of both 1,6-dibromo- and 1,6-diiodohexane *in the absence of any added proton or deuteron donor* are that no halogen-

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Table 1. Coulometric Data and Product Distributions for Electrolytic Reduction of 1,6-Dibromohexane in DMF Containing 0.10 M TMAP at Reticulated Vitreous Carbon at −1.95 V

Concn, mM	n	product distribution,[a] %									
		1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	others	total
5	2.33	45	33	14	3	tr	–	tr	1	–	96
10	2.18	39	34	13	5	1	tr	2	3	–	97
20	2.10	38	29	16	5	2	tr	3	4	–	97
5[b]	–	34	15	4	3	–	–	14	31	–	101
5[c]	2.70	64	2	1	2	–	–	–	–	33[f]	102
5[d]	1.75	30	23	9	2	2	tr	4	8	23[g]	101
5[e]	–	89	5	–	2	tr	–	–	–	–	96

[a] **1** = *n*-Hexane, **2** = 1-hexene, **3** = 1,5-hexadiene, **4** = cyclohexane, **5** = *n*-dodecane, **6** = 1-dodecene, **7** = 1-hexanol, **8** = 5-hexen-1-ol, tr = trace. [b] 1 M D_2O was present. [c] 50 mM Diethyl malonate-d_2 was present. [d] 1 M Acetonitrile-d_3 was present. [e] 50 mM 1,1,1,3,3,3-Hexafluoro-2-propanol was present. [f] Diethyl *n*-hexylmalonate-*d*. [g] A mixture of 1,1-dideuterioheptyl cyanide (14%) and 7-cyano-7,7-dideuterio-1-heptene (9%).

Table 2. Coulometric Data and Product Distributions for Electrolytic Reduction of 1,6-Diiodohexane at Reticulated Vitreous Carbon in DMF Containing 0.10 M TMAP

E, V	concn, mM	n	product distribution,[a] %											
			1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	others	total
−1.70	5	2.11	34	31	13	6	4	2	2	2	1	–	–	95
−1.70	10	1.89	34	34	6	3	11	5	1	1	5	1	–	101
−1.70	20	1.95	30	28	7	4	12	4	–	1	8	2	–	96
−1.95	20	2.07	32	28	7	7	11	3	2	4	7	1	–	102
−1.70[b]	5	1.80	25	27	8	4	<1	–	8	25	–	–	–	98
−1.70[c]	5	2.40	29	16	6	2	2	–	–	–	–	–	41[f]	96
−1.70[d]	5	2.00	22	22	6	3	2	tr	1	2	–	–	44[g]	102
−1.70[e]	5	–	62	15	3	5	6	–	–	–	3	–	–	94

[a] **1** = *n*-Hexane, **2** = 1-hexene, **3** = 1,5-hexadiene, **4** = cyclohexane, **5** = *n*-dodecane, **6** = 1-dodecene, **7** = 1-hexanol, **8** = 5-hexen-1-ol, **9** = *n*-octadecane, **10** = 1-octadecene, tr = trace. [b] 1 M D_2O was present. [c] 50 mM Diethyl malonate-d_2 was present. [d] 1 M Acetonitrile-d_3 was present. [e] 50 mM 1,1,1,3,3,3-Hexafluoro-2-propanol was present. [f] Diethyl *n*-hexylmalonate-*d*. [g] A mixture of 1,1-dideuterioheptyl cyanide (29%) and 7-cyano-7,7-dideuterio-1-heptene (15%).

Table 3. Coulometric Data and Product Distributions for Electrolytic Reduction of 1-Bromo-6-chlorohexane in DMF Containing 0.10 M TMAP at Reticulated Vitreous Carbon at −1.95 V

Concn, mM	n	product distribution,[a] %						
		11	**12**	**13**	**7**	**8**	others	total
5	1.26	56	33	2	3	4	–	98
10	1.20	64	28	5	1	4	–	102
5[b]	1.01	48	29	tr	8	16	–	101
5[c]	1.38	65	–	–	–	–	32[f]	97
5[d]	0.97	50	25	1	1	4	20[g]	101
5[e]	–	93	2	–	1	–	–	96

[a] **11** = 1-Chlorohexane, **12** = 6-chloro-1-hexene, **13** = 1,12-dichlorododecane, **7** = 1-hexanol, **8** = 5-hexen-1-ol, tr = trace. [b] 1 M D_2O was present. [c] 50 mM Diethyl malonate-d_2 was present. [d] 1 M Acetonitrile-d_3 was present. [e] 50 mM 1,1,1,3,3,3-Hexafluoro-2-propanol was present. [f] Diethyl (6-chlorohexyl)malonate-*d*. [g] 7-Chloro-1,1-dideuterioheptyl cyanide.

Table 4. Coulometric Data and Product Distributions for Electrolytic Reduction of 1-Chloro-6-iodohexane at Reticulated Vitreous Carbon in DMF Containing 0.10 M TMAP

E, V	concn, mM	n	product distribution,[a] %						
			11	**12**	**13**	**7**	**8**	others	total
−1.70	5	1.13	65	25	4	tr	2	–	96
−1.70	10	1.06	51	20	25	1	1	–	98
−1.95	10	1.15	47	27	22	1	2	–	99
−1.70[b]	5	1.13	63	27	3	3	4	–	100
−1.70[c]	5	0.75	49	9	10	–	–	33[f]	101
−1.70[d]	5	1.00	41	21	13	1	4	22[g]	102
−1.70[e]	5	–	65	25	4	–	–	–	94

[a] **11** = 1-Chlorohexane, **12** = 6-chloro-1-hexene, **13** = 1,12-dichlorododecane, **7** = 1-hexanol, **8** = 5-hexen-1-ol, tr = trace. [b] 1 M D_2O was present. [c] 50 mM Diethyl malonate-d_2 was present. [d] 1 M Acetonitrile-d_3 was present. [e] 50 mM 1,1,1,3,3,3-Hexafluoro-2-propanol was present. [f] Diethyl (6-chlorohexyl)malonate-*d*. [g] 7-Chloro-1,1-dideuterioheptyl cyanide.

containing compounds are seen and that the major products are *n*-hexane and 1-hexene. On the other hand, for 1-bromo-6-chloro- and 1-chloro-6-iodohexane, each of which possesses a nonreducible carbon–chlorine bond, the principal products obtained *in the absence of an added proton or deuteron donor* are 1-chlorohexane, 6-chloro-1-hexene, and 1,12-dichlorododecane. All electrolyses of 1,6-dibromo- and 1-bromo-6-chlorohexane were carried out at −1.95 V, whereas most of the reductions of 1,6-diiodo- and 1-chloro-6-iodohexane were conducted at −1.70 V; however, as indicated in Tables 2 and 4, a few experiments involving the latter pair of compounds were performed at −1.95 V, but no significant difference in the results was observed.

In earlier studies of the electrochemistry of 1,4- and 1,5-dihaloalkanes conducted in our laboratory,[2,3] 4-chloro-1-butene (in the presence of 1-chlorobutane) and 5-chloro-1-pentene (in the presence of 1-chloropentane) were undetected because they could not be resolved from the corresponding 1-chloroalkane under certain gas chromatographic conditions. For example, for electrolyses of 1-chloro-5-iodopentane at reticulated vitreous carbon in DMF containing 0.050 M TMAP at −1.70 V, it was reported[3] that 1-chloropentane was formed in 76% yield. However, on repeating this experiment, we found with the aid of GC-MS that a nearly one-to-one mixture of 1-chloropentane and 5-chloro-1-pentene is actually obtained. Accordingly, when 1-chlorobutane or 1-chloropentane was listed as a product in those previous investigations, a mixture of 1-chlorobutane and 4-chloro-1-butene or 1-chloropentane and 5-chloro-1-pentene was actually present.

Mechanistic Aspects of the Electrolysis of 1,6-Dihalohexanes. In parallel with the mechanisms proposed previously for the reduction of 1,4- and 1,5-dihaloalkanes at carbon cathodes,[2,3] the following sequence of reactions (where X = Br or I) can account for the formation of *n*-hexane from electrolyses of 1,6-diiodo- and 1,6-dibromohexane:

$$\mathrm{X(CH_2)_6X + e^- \longrightarrow X(CH_2)_6^{\bullet} + X^-}$$

$$\mathrm{X(CH_2)_6^{\bullet} + e^- \longrightarrow X(CH_2)_6^-}$$

$$\mathrm{X(CH_2)_6^- + H_2O \longrightarrow X(CH_2)_5CH_3 + OH^-}$$

Under the conditions of the present work, we have found that the cyclic voltammetric peak potentials for reduction of 1-iodo- and 1-bromohexane are −1.42 and −1.70 V, respectively, and that both compounds undergo two-electron reductions at glassy carbon cathodes in DMF–TMAP. Consequently, at the potentials (−1.70 and −1.95 V) that we employed to electrolyze the 1,6-dihalohexanes, 1-bromo- and 1-iodohexane are reduced to *n*-hexane:

$$\mathrm{X(CH_2)_5CH_3 + 2\,e^- + H_2O \longrightarrow CH_3(CH_2)_4CH_3 + X^- + OH^-}$$

Hydroxide ion, resulting from the deprotonation of water (present as an adventitious impurity in the solvent-supporting electrolyte) by electrogenerated carbanions, can dehydrohalogenate 1-bromo- or 1-iodohexane to form 1-hexene via an E2 reaction,

$$\mathrm{X(CH_2)_5CH_3 + OH^- \xrightarrow{E2} CH_2{=}CH(CH_2)_3CH_3 + H_2O + X^-}$$

or hydroxide ion can attack 1-bromo- or 1-iodohexane to afford 1-hexanol by an S_N2 reaction:

$$\mathrm{X(CH_2)_5CH_3 + OH^- \xrightarrow{S_N2} HO(CH_2)_5CH_3 + X^-}$$

However, the latter process becomes important only for high concentrations of water, which accounts for our observation that the yield of 1-hexene is always much higher than that of 1-hexanol. We suggest that 1,5-hexadiene is formed through a pair of E2 reactions involving the attack of hydroxide ions on the starting material:

$$\mathrm{X(CH_2)_6X + OH^- \xrightarrow{E2} X(CH_2)_4CH{=}CH_2 + H_2O + X^-}$$

$$\mathrm{X(CH_2)_4CH{=}CH_2 + OH^- \xrightarrow{E2} CH_2{=}CH(CH_2)_2CH{=}CH_2 + H_2O + X^-}$$

Moreover, 6-iodo- and 6-bromo-1-hexene involved in the preceding set of reactions are electroactive at the potentials used to electrolyze the 1,6-dihalohexanes; the cyclic voltammetric peak potentials for the two-electron reduction of 6-iodo- and 6-bromo-1-hexene in DMF–TMAP are −1.40 and -1.70 V, respectively. Accordingly, the following reaction must take place:

$$\mathrm{X(CH_2)_4CH{=}CH_2 + 2\,e^- + H_2O \longrightarrow CH_3(CH_2)_3CH{=}CH_2 + OH^- + X^-}$$

Along with the E2 reaction between OH^- and a 6-halo-1-hexene, OH^- can attack 6-iodo- or 6-bromo-1-hexene via an S_N2 process to yield 5-hexen-1-ol. We believe that the small amount of cyclohexane seen in electrolyses of 1,6-diiodo- and 1,6-dibromohexane arises from intramolecular cyclization of the 6-iodo- or 6-bromohex-1-yl carbanion.

In previous studies of the electrochemical reduction of 1,4-diiodobutane[2] and 1,5-diiodopentane at carbon cathodes,[3] it was found that dimeric, trimeric, and even tetrameric products arise from radicals formed by one-electron reduction of carbon–iodine bonds. Therefore, to explain the appearance of significant yields of the dimeric species, *n*-dodecane and 1-dodecene, from electrolyses of 1,6-diiodohexane, we suggest that coupling of electrogenerated 6-iodohex-1-yl radicals occurs to form 1,12-diiododecane,

$$\mathrm{2\,I(CH_2)_6^{\bullet} \longrightarrow I(CH_2)_{12}I}$$

followed by electrolytic reduction of 1,12-diiodododecane to 1-iodododecane:

$$\mathrm{I(CH_2)_{12}I + 2\,e^- + H_2O \longrightarrow I(CH_2)_{11}CH_3 + OH^- + I^-}$$

Any disproportionation of electrogenerated 6-iodohex-1-yl radicals would lead to 1-iodohexane and 6-iodo-1-hexene, both of which could undergo two-electron reduction. Once 1-iodododecane is produced, it can undergo further reduction and protonation to give *n*-dodecane

$$\mathrm{I(CH_2)_{11}CH_3 + 2\,e^- + H_2O \longrightarrow CH_3(CH_2)_{10}CH_3 + OH^- + I^-}$$

or an E2 reaction to give 1-dodecene:

$$\mathrm{I(CH_2)_{11}CH_3 + OH^- \xrightarrow{E2} CH_2{=}CH(CH_2)_9CH_3 + H_2O + I^-}$$

Alternatively, *n*-dodecane can arise by one-electron scission of each carbon-iodine bond of 1,12-diiodododecane

$$\mathrm{I(CH_2)_{12}I + 2\,e^- + 2\,H^{\bullet} \longrightarrow CH_3(CH_2)_{10}CH_3 + 2\,I^-}$$

or by one-electron reduction of 1-iodododecane, with the solvent serving as a hydrogen atom donor. Moreover, 1-iodododecane can react with hydroxide ion to generate 1-dodecene. Formation of small amounts of trimeric products (*n*-octadecane and 1-octadecene) can be rationalized in terms of reactions that are extensions of those just described. Analogues of the preceding reactions for the formation of dimeric and trimeric products from the reduction of 1,6-dibromohexane are of minor importance.

In writing a mechanism for the reduction of 1-bromo-6-chloro- and 1-chloro-6-iodohexane (which behave, respectively, as an alkyl bromide and iodide, owing to their electroinactive carbon–chlorine bonds), we propose that 1-bromo-6-chlorohexane is electrolytically reduced to the 6-chlorohex-1-yl carbanion which can be protonated to afford 1-chlorohexane:

$$\mathrm{Br(CH_2)_6Cl + 2\,e^- + H_2O \longrightarrow CH_3(CH_2)_5Cl + OH^- + Br^-}$$

As before, hydroxide can engage in an E2 reaction with 1-bromo-6-chlorohexane to form 6-chloro-1-hexene,

$$\mathrm{Br(CH_2)_6Cl + OH^- \xrightarrow{E2} CH_2{=}CH(CH_2)_4Cl + H_2O + Br^-}$$

which, in turn, can react with OH^- (at high water concentrations) to form 5-hexen-1-ol.

Although the preceding reactions involved in the reduction of 1-bromo-6-chlorohexane are expected to occur for electrolyses of 1-chloro-6-iodohexane, we believe that the latter starting material also accepts one electron to yield the 6-chlorohex-1-yl radical which can (a) dimerize to give 1,12-dichlorododecane, (b) disproportionate to afford 1-chlorohexane and 6-chloro-1-hexene, or (c) accept a hydrogen atom from the solvent to give 1-chlorohexane.

To verify that electrogenerated carbanions are involved as intermediates in the reduction of 1,6-dihalohexanes, we performed electrolyses in which D_2O, $CD_2(COOC_2H_5)_2$, CD_3CN, and $(CF_3)_2CHOH$ were added to serve as deuteron or proton donors; the last four entries in Tables 1–4 give the results of these studies. In addition, because *n*-hexane and 1-hexene are the two dominant products derived from the reduction of 1,6-dibromo- and 1,6-diiodohexane, we utilized GC-MS to measure the extent of deuterium incorporation in the *n*-hexane and 1-hexene that were formed in the electrolyses of these two 1,6-dihalohexanes in the presence of D_2O, CD_3CN, and $CD_2(COOC_2H_5)_2$. Table 5 shows the results of these latter experiments, and these data have been corrected for the natural isotopic abundances of ^2H and ^{13}C. We could not use the same approach to determine the deuterium incorporated into the 1-chlorohexane and

Table 5. Mass Spectrometric Data for $C_6H_{14}^+$, $C_6H_{13}D^+$, and $C_6H_{12}D_2^+$ Derived from *n*-Hexane and for $C_6H_{12}^+$ and $C_6H_{11}D^+$ Derived from 1-Hexene Formed from Electrolyses of 1,6-Dibromohexane at −1.95 V and of 1,6-Diiodohexane at −1.70 V at Reticulated Vitreous Carbon in DMF Containing 0.10 M TMAP and Various Deuterium Sources

	relative abundance of molecular ions, %				
	from *n*-hexane			from 1-hexene	
conditions	$C_6H_{14}^+$	$C_6H_{13}D^+$	$C_6H_{12}D_2^+$	$C_6H_{12}^+$	$C_6H_{11}D^+$
5 mM 1,6-dibromohexane + 1 M D_2O	23	49	28	47	53
5 mM 1,6-dibromohexane + 1 M CD_3CN	27	50	23	57	43
5 mM 1,6-dibromohexane + 50 mM diethyl malonate-d_2	90	10	0	–	–
5 mM 1,6-diiodohexane + 1 M D_2O	56	39	5	81	19
5 mM 1,6-diiodohexane + 1 M CD_3CN	44	51	5	73	27
5 mM 1,6-diiodohexane + 50 mM diethyl malonate-d_2	88	11	1	100	0

6-chloro-1-hexene arising from electrolyses of 1-bromo-6-chloro- and 1-chloro-6-iodohexane in the presence of deuterium-labeled reagents because of the low abundances (due to loss of HCl) of the molecular ions derived from these two products. Similarly, the degree of deuterium incorporation into 1-hexanol and 5-hexen-1-ol could not be assessed because the molecular ions for these species were in low abundance (due to the loss of H_2O).

In general, as the last four entries in Tables 1−4 reveal, the presence of 1 M D_2O increases the yields of 1-hexanol and 5-hexen-1-ol (probably as $C_6H_{13}OD$ and $CH_2{=}CH(CH_2)_4OD$, respectively). More importantly, clear evidence for the intermediacy of carbanions in electrolyses of 1,6-dibromo- and 1,6-diiodohexane is seen in Table 5. When these two compounds were reduced in DMF−TMAP containing 1 M D_2O, 77% of the *n*-hexane and 53% of the 1-hexene formed from 1,6-dibromohexane contained deuterium, whereas 44% of the *n*-hexane and 19% of the 1-hexene obtained from 1,6-diiodohexane contained deuterium. This difference suggests that the electrolytic reduction of 1,6-diiodohexane probably involves radical as well as carbanionic intermediates.

When 50 mM diethyl malonate-d_2 is present during electrolyses of 1,6-dibromo- and 1-bromo-6-chlorohexane, the yields of *n*-hexane and 1-chlorohexane rise at the expense of 1-hexene and 6-chloro-1-hexene, respectively, and substantial amounts of diethyl *n*-hexylmalonate-*d* and diethyl (6-chlorohexyl)malonate-*d* are found. Diethyl malonate-d_2 has little tendency to donate a deuteron to electrogenerated carbanions, as indicated in Table 5, but it does block the E2 processes that lead to 1-hexene and 6-chloro-1-hexene by reacting with OH^- (from the deprotonation of water by carbanions) which does promote the dehydrohalogenations of 1-bromo- and 1-iodohexane and of 1-bromo-6-chloro- and 1-chloro-6-iodohexane. However, the conjugate base of diethyl malonate-d_2 can react nucleophilically with 1-bromo- and 1-iodohexane to give diethyl *n*-hexylmalonate-*d* or with 1-bromo-6-chloro- and 1-chloro-6-iodohexane to afford diethyl (6-chlorohexyl)-malonate-*d*.

Tables 1 through 4 reveal that one of the interesting aspects of the use of CD_3CN in electrolyses of the 1,6-dihalohexanes is the appearance of significant quantities of 1,1-dideuterioheptyl cyanide, 7-cyano-7,7-dideuterio-1-heptene, and 7-chloro-1,1-dideuterioheptyl cyanide. We believe that these adducts arise in two ways. First, with 1,6-dibromo- and 1-bromo-6-chlorohexane (which appear to undergo reduction to carbanion intermediates only), CD_3CN can act as a deuteron donor, and the resulting $^-CD_2CN$ can subsequently attack 1-bromohexane, 6-bromo-1-hexene, and 1-bromo-6-chlorohexane. Second, with 1,6-diiodo- and 1-chloro-6-iodohexane (which appear to undergo reduction to both radicals and carbanions), CD_3CN can serve as both a deuterium ion and atom donor; the resulting $^-CD_2CN$ reacts as just stated and $^\bullet CD_2CN$ can couple with an *n*-hexyl, 1-hexen-6-yl, or 6-chlorohex-1-yl radical. This ability of CD_3CN (or CH_3CN) to function as both a deuterium (or hydrogen) ion or atom donor is well documented in the electrochemical literature.[14−22]

As a proton donor for electrogenerated carbanions, 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) is similar in its behavior to diethyl malonate-d_2. However, although HFIP blocks dehydrohalogenation reactions effectively, by intercepting OH^- arising from the deprotonation of water by carbanions, HFIP forms no adducts with any of the starting materials or products.

Consequently, for reduction of 1,6-dibromo- and 1,6-diiodohexane in the presence of HFIP, the yields of *n*-hexane are significantly higher than those obtained from electrolyses done in the presence of diethyl malonate-d_2. Similarly, the yields of 1-chlorohexane obtained from electrolyses of 1-bromo-6-chloro- and 1-chloro-6-iodohexane in the presence of HFIP are greater than those found when diethyl malonate-d_2 is present. Finally, because the reduction of 1,6-diiodo- and 1-chloro-6-iodohexane leads to both radical and carbanion intermediates, the effect of HFIP on the electrochemical behavior of these compounds is not as pronounced as is seen with the corresponding bromo analogues.

In summary, for the reduction of 1,6-dibromo- and 1-bromo-6-chlorohexane, we conclude that electrogenerated carbanions are involved virtually exclusively as intermediates, whereas our findings indicate that alkyl radicals and carbanions are both involved as intermediates in the electrolysis of 1,6-diiodo- and 1-chloro-6-iodohexane.

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