Electrochemical Reduction of 2-Iodooctane and 2-Bromooctane at Mercury Cathodes in Dimethylformamide

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Received March 29, 1982

In dimethylformamide containing tetraalkylammonium perchlorates, a pulse polarogram for 2-iodooctane exhibits a pair of waves of identical height, attributed to stepwise reduction to the *sec*-octyl radical and carbanion, respectively. In contrast, 2-bromooctane gives a single pulse polarographic wave the height of which is equal to the sum of the two waves for the alkyl iodide. At potentials on the first wave, large-scale electrolysis of 2-iodooctane results in mercury-stabilized *sec*-octyl radicals via one-electron cleavage of the carbon–iodine bond; the radicals can disproportionate to yield octane along with 1-octene or 2-octene, can couple to give 7,8-dimethyltetradecane, or can react with mercury to afford di-*sec*-octylmercury. At potentials on the second wave, reduction of 2-iodooctane leads mainly to the *sec*-octyl carbanion; octane is produced by proton transfer from water (in the solvent-supporting electrolyte) to the carbanion, and olefins arise from hydroxide-promoted (E2) dehydrohalogenation of starting material. Excess proton donor (water or diethyl malonate) blocks the E2 process, increases the quantity of octane, lowers the yield of octenes, and raises the coulometric *n* value nearly to 2. However, at potentials on the second wave, a small amount of di-*sec*-octylmercury is formed, indicating that reduction of 2-iodooctane proceeds via the *sec*-octyl radical; 7,8-dimethyltetradecane is produced by radical coupling, and some of the octane and octenes apparently originate via radical disproportionation. For reduction of 2-bromooctane, the yields of octane and octenes are comparable to those derived from 2-iodooctane under similar conditions. No di-*sec*-octylmercury is produced from the bromo compound; little, if any, 7,8-dimethyltetradecane is formed; and the coulometric *n* value is higher than that for 2-iodooctane.

Recent publications from our laboratory[1-3] have dealt with the electrochemical behavior of primary alkyl monoiodides and monobromides at mercury cathodes in dimethylformamide containing tetraalkylammonium perchlorates. In addition, the electrochemistry of primary alkyl halides has been treated in numerous other articles[4-6] and books.[7-10]

For a simple alkyl iodide, such as 1-iodododecane, the pathway for reduction at mercury electrodes as well as the identities and yields of products depends on the potential of the cathode, on the time scale[11] of the electrolysis, and on the amount of water in the solvent-supporting electrolyte system. In dimethylformamide containing tetramethylammonium perchlorate, an ordinary dc polarogram for reduction of 1-iodododecane exhibits two waves; an anomalous current maximum appears on the rising portion of the second wave. At potentials positive with respect to the polarographic maximum, the alkyl iodide accepts one electron to yield a decyl radical which becomes an adsorbed decylmercury radical and, in approximately 1 ms,[12] the adsorbed organomercury radicals disproportionate to form didecylmercury. Regardless of the time scale of the electrolysis or the water content of the solvent-supporting electrolyte, didecylmercury is the only product obtained at these potentials. However, at potentials negative with respect to the polarographic maximum, transfer of two electrons to 1-iodododecane is predominant, though there is evidence that the reduction does proceed through a radical intermediate. Once formed, the decyl carbanion accepts a proton from water present as an impurity to give decane and hydroxide ion; then the hydroxide ion can subsequently attack a molecule of unreduced 1-iodododecane to produce 1-decanol (S_N2 displacement) or to yield 1-decene (E2 elimination). If the concentration of water in the solvent-supporting electrolyte is moderately high (approximately 0.05 M)[13] or if the time scale of electrolysis is relatively long,[11] the extent of interaction between hydroxide ion and unreduced 1-iodododecane is appreciable, and the number of electrons transferred to each molecule of the alkyl iodide may appear to be unity. On the other hand, if the concentration of water is relatively low (<0.002 M) or if the time scale of the electrolysis is short, the chemical reaction between hydroxide ion and unreduced 1-iodododecane is insignificant, and the coulometric *n* value approaches 2.

In contrast to 1-iodododecane, polarographic reduction of 1-bromodecane shows only a single wave at potentials that correspond to the formation of carbanionic intermediates. Accordingly, the electrochemistry of primary alkyl monobromides at mercury in dimethylformamide containing tetraalkylammonium salts closely resembles the behavior of primary alkyl monoiodides at potentials negative with respect to the polarographic maximum.

Aside from measurements of polarographic half-wave potentials for some secondary and tertiary alkyl monohalides,[10] there is little, if any, published information about the products derived from the electrolysis of these sub-

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[1] McNamee, G. M; Willett, B. C.; La Perriere, D. M.; Peters, D. G. *J. Am. Chem. Soc.* **1977**, *99*, 1831–1835.

[2] La Perriere, D. M.; Willett, B. C.; Carroll, W. F., Jr.; Torp, E. C.; Peters, D. G. *J. Am. Chem. Soc.* **1978**, *100*, 6293–6294.

[3] La Perriere, D. M.; Carroll, W. F., Jr.; Willett, B. C.; Torp, E. C.; Peters, D.G. *J. Am. Chem. Soc.* **1979**, *101*, 7561–7568.

[4] Wagenknecht, J. H. *J. Electroanal. Chem.* **1974**, *52*, 489–492.

[5] Dougherty, J. A.; Diefenderfer, A. J. *J. Electroanal. Chem.* **1969**, *21*, 531–534.

[6] Sease, J. W.; Reed, R. C. "Abstracts"; Electrochemical Society Meeting, New York, May, 1969; No. 134, p 328.

[7] Mann, C. K.; Barnes, K. K. "Electrochemical Reactions in Nonaqueous Systems"; Marcel Dekker: New York, 1970; pp 201–205.

[8] Fry, A. J. "Synthetic Organic Electrochemistry"; Harper & Row: New York, 1972; pp 170–173.

[9] Casanova, J.; Eberson, L. In "The Chemistry of Functional Groups. The Chemistry of the Carbon-Halogen Bond"; Patai, S., Ed.; Wiley: London, 1973; Part 2, Chapter 15, pp 979–1047.

[10] Hawley, M. D. In "Encyclopedia of Electrochemistry of the Elements"; Bard, A. J., Lund, H., Ed.; Marcel Dekker: New York, 1980; Vol. 14, Chapter 1, pp 6–19.

[11] The time scale of the electrolysis refers to the total elapsed time from the initiation of the voltage waveform to its termination. An experiment of relatively long time scale refers to an electrolysis lasting approximately 15 min at a mercury pool, whereas experiments of short duration refer, for example, to chronocoulometry and pulse polarography which are performed with microelectrodes.

[12] Willett, B. C.; Peters, D. G. *J. Electroanal. Chem.* **1981**, *123*, 291–306.

[13] We have found that the concentration of water is approximately 0.05 M in solvent-supporting electrolyte which is not subjected to any special drying procedure; this concentration is at least 10 times that of the starting material. However, the water content can be lowered to approximately 0.002 M if the solvent-supporting electrolyte is brought into contact with activated alumina.

0022-3263/82/1947-3397$01.25/0

stances or about the mechanism of the reduction of these compounds at mercury cathodes. In the present paper, we report the results of an investigation of the electrochemical behavior of 2-iodooctane and 2-bromooctane at mercury electrodes in dimethylformamide containing tetraalkylammonium salts.

Experimental Section

Reagents. Tetramethylammonium perchlorate and tetra-*n*-butylammonium perchlorate, both purchased from the G. Frederick Smith Chemical Co., were employed without further purification as supporting electrolytes. After being vacuum distilled, commericially available 2-iodooctane (Columbia Organic Chemical Co.) and 2-bromooctane (J. T. Baker Chemical Co.) were utilized for electrochemical experiments. Mercury (Ventron, triply distilled) was used as received.

Dimethylformamide employed as solvent was either Fisher Spectranalyzed material or Matheson Coleman & Bell reagent; it was distilled twice at reduced pressure (2–3 torr) from calcium hydride and from barium oxide and then was dried over Linde 4A molecular sieves. Matheson prepurified nitrogen (99.998%) was used to deaerate solutions.

Instrumentation and Procedures. Descriptions of the electrolysis cells and instrumentation for conventional and pulse polarography and for cyclic voltammetry as well as procedures for controlled-potential electrolyses can be found elsewhere.[3] All potentials are quoted with respect to a reference electrode consisting of a saturated cadmium amalgam in contact with dimethylformamide saturated with both cadmium chloride and sodium chloride;[14,15] this electrode has a potential of −0.75 V vs. the aqueous saturated calomel electrode.

A dual-column Hewlett-Packard Model 5712A gas chromatograph equipped with a thermal conductivity detector was employed for the separation and determination of electrolysis products; columns used in the present work were similar to those described previously.[3] Gas chromatographic peak areas were measured with the aid of a Hewlett-Packard Model 3380S integrator; all yields reported in this paper are absolute percentages (determined with respect to a known amount of phenylcyclohexane added as an internal standard) of starting material incorporated into a given product. Data in the tables show that the total recovery of products obtained at the least negative potentials is noticeably below the 100% level, whereas the recovery is close to 100% at the most negative potentials; this difference is due to the fact that electrolyses performed at the least negative potentials take longer to complete than those at the most negative potentials, so the loss of volatile hydrocarbon products in the nitrogen stream used to deaerate a solution is more serious in the former than in the latter experiments. Mass spectral studies of individual electrolysis products were done with a Hewlett-Packard Model 5992A gas chromatograph–mass spectrometer system or with a Varian CH-7 spectrometer.

Synthesis of 1,1,1,3,3-Pentadeuterio-2-iodooctane. A mixture of 11 mL of 2-octanone, 50 mL of D_2O, and a small amount (0.5–1.0 g) of potassium carbonate was refluxed and stirred continuously for 4 h; twice, after this treatment, the organic layer was separated and refluxed with fresh portions of D_2O and potassium carbonate for another 4 h. The resulting $C_5H_{11}CD_2COCD_3$ was separated from the aqueous layer, washed with D_2O, dried over anhydrous calcium chloride, and distilled at atmospheric pressure (bp 170–172 °C). Proton NMR spectroscopy confirmed indirectly that there was more than 98% deuteration at the 1- and 3-positions.

Nine milliliters of the previously obtained $C_5H_{11}CD_2COCD_3$, dissolved in approximately 10 mL of dry tetrahydrofuran (distilled from benzophenone and potassium), was added dropwise at 0 °C over a 15-min period to 50 mL of dry tetrahydrofuran containing 2 g of lithium aluminum hydride. After being stirred for 2 h, the mixture was treated with water; the tetrahydrofuran phase was dried over anhydrous sodium sulfate, and $C_5H_{11}CD_2CH(OH)CD_3$ was separated by distillation at atmospheric pressure (bp 171–174 °C).

In 70 mL of dry pyridine (refluxed over barium oxide for 30 min and then distilled) contained in a glass-stoppered 125-mL Erlenmeyer flask was dissolved 4.5 g of the deuterated alcohol, $C_5H_{11}CD_2CH(OH)CD_3$. This mixture was cooled to 0 °C and was treated with 14 g of tosyl chloride.[16] After dissolution of the tosyl chloride was complete, the flask was placed in a refrigerator for approximately 20 h, during which time needles of pyridine hydrochloride formed. Then the contents of the flask were poured with stirring over 300 g of an ice–water mixture. Three extractions of the aqueous phase were done with diethyl ether. Then the ether extracts were combined and dried over anhydrous sodium sulfate–potassium carbonate; the ether was evaporated, leaving oily $C_5H_{11}CD_2CH(OTs)CD_3$.

This crude tosylate was dissolved in a minimal volume of acetone; the solution was added to 60 mL of acetone containing 12 g of sodium iodide and the mixture was stirred overnight. Then the solution was extracted with diethyl ether, and the ether extract was washed twice with water and dried over anhydrous calcium chloride. Finally, the ether was evaporated and the residue was distilled (bp 90 °C) at reduced pressure (14 torr); the alkyl iodide was found by means of gas chromatography to be 99.5% pure. Its isotopic composition was determined with the aid of a mass spectrum recorded at 70 eV, relative abundances being reported in parentheses: *m/e* 245 (1.3), 119 (17), 118 (100), 117 (25), and 116 (6.5); from the preceding data, we estimated that the alkyl iodide consisted of 75–80% 1,1,1,3,3-pentadeuterio-2-iodooctane.

Product Identification. Octane, 1-octene, and *cis*- and *trans*-2-octene (hereafter referred to collectively as 2-octene[17]) were identified by comparison of their gas chromatographic retention times with those of commercially available authentic samples. Because di-*sec*-octylmercury is thermally unstable[18] under the conditions of a gas chromatographic analysis, yields of this product were determined in a special way. To a portion of the ether extract containing all of the electrolysis products was added a saturated solution of bromine in glacial acetic acid; this procedure converts di-*sec*-octylmercury quantitatively to 2-bromooctane which can be determined by means of gas chromatography. Because our experiments always involved complete reduction of either 2-iodooctane or 2-bromooctane, any 2-bromooctane seen after the treatment with the bromine–glacial acetic acid reagent is a unique measure of the quantity of di-*sec*-octylmercury actually formed in an electrolysis.

Another electrolysis product, 7,8-dimethyltetradecane, was identified by comparison of its gas chromatographic retention time and mass spectrum with those of an authentic sample. We prepared this compound by refluxing overnight 6.4 g of sodium and 25 g of 2-bromooctane dissolved in diethyl ether. Excess sodium metal was destroyed by addition of methanol and *tert*-butyl alcohol to the reaction mixture. Then the ether layer was washed with distilled water and dried over anhydrous magnesium sulfate. After the ether was evaporated, the residue was distilled twice under reduced pressure (12 torr) to separate the desired compound ($C_{16}H_{34}$, bp 132–136 °C) from starting material ($C_8H_{17}Br$, bp 69–70 °C). Gas chromatographic analysis of the compound (obtained both by chemical synthesis and by electrolysis) revealed that it consisted of a mixture of *dl*- and *meso*-7,8-dimethyltetradecane. Mass spectra obtained at 70 eV for the authentic mixture of diastereomers yielded the following results: *m/e* 226 (2), 113 (11), 112 (60), 71 (65), 57 (100), and 43 (80).

Results and Discussion

Polarographic and Voltammetric Behavior of 2-Iodooctane and 2-Bromooctane. Conventional dc po-

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[14] Marple, L. W. *Anal. Chem.* **1967**, *39*, 844–846.

[15] Hall, J. L.; Jennings, P. W. *Anal. Chem.* **1976**, *48*, 2026–2027.

[16] Fieser, L. F.; Fieser, M. "Reagents for Organic Synthesis"; Wiley: New York, 1967; Vol. 1, pp 1179–1181.

[17] In most of our experiments, gas chromatographic columns employed to separate electrolysis products did not resolve *cis*- and *trans*-2-octene, so that only the sum of yields of the two isomers is tabulated in this paper. However, we have utilized a 14 ft × 1/8 in. stainless-steel column packed with 15% Carbowax 20M-TPA on 80–100-mesh Chromosorb WHP to separate and quantitate the isomers of 2-octene formed in electrolyses at potentials corresponding to the plateau regions of both the first and second pulse polarographic waves; the ratio of *cis*- to *trans*-2-octene was found to be close to 1:4 regardless of potential.

[18] Marvel, C. S.; Calvery, H. O. *J. Am. Chem. Soc.* **1923**, *45*, 820–823.

Table I. Coulometric Data and Product Distributions for Controlled-Potential Electrolytic Reduction of 2-Iodooctane at Mercury in Dimethylformamide

conditions[a]	wave	*n* value	product distribution, % octane	1-octene	2-octene	di-*sec*-octylmercury	7,8-dimethyltetradecane
(1) 0.1 M Tetramethylammonium Perchlorate							
0.0025 M RI	first	0.95	24	12	10	24	17
	second	1.08	52	12	24	6	5
0.001 M RI,	first	0.94	24	10	8	29	18
1 M H_2O	second	1.71	71	4	8	5	3
0.001 M RI,	first	0.92	22	11	10	24	17
0.005 M DEM	second	1.72	79			1	3
(2) 0.1 M Tetra-*n*-butylammonium Perchlorate							
0.0025 M RI	first	0.96	31	14	10	5	26
	second	1.12	41	14	21		17
0.012 M RI	first[b]	0.93	32	13	8	5	26
	second[c]	1.17	36	9	17		28
0.001 M RI,	first	0.92	23	11	10	7	23
1 M H_2O	second	1.73	71	5	9		5
0.001 M RI,	first	0.90	23	12	11	4	27
0.005 M DEM	second	1.83	90				6

[a] RI = 2-iodooctane, DEM = diethyl malonate. [b] In this experiment, 2-octanol was obtained in 1% yield. [c] In this experiment, 2-octanol was obtained in 3% yield.

larograms recorded at room temperature for 2-iodooctane in dimethylformamide containing 0.1 M tetramethylammonium perchlorate bear a close resemblance to those for 1-iododecane published earlier.[1,3] It appears that the secondary alkyl iodide undergoes stepwise reduction; but the polarographic waves are not clearly delineated, and the large current maximum which rises out of the plateau of the first wave and which obscures the rising portion of the second wave prevents us from reporting meaningful half-wave potentials. When 0.1 M tetra-*n*-butylammonium perchlorate is used as supporting electrolyte, the polarographic waves as well as the current maximum shift toward more negative potentials; changing the identity of the tetraalkylammonium salt has been noted to cause the same effect in previous studies of other alkyl halides.[1,19–21] In constrast to the behavior of 2-iodooctane, polarograms for the reduction of 2-bromooctane exhibit just one irreversible wave without any current maximum.

Cyclic voltammograms for 2-iodooctane at a hanging mercury drop cathode show the same features as those for 1-iododecane described in our earlier publication.[3] Again, the two-step reduction of the secondary alkyl iodide reveals itself and, at scan rates less than 500 mV/s, an inverted wave is seen on the reverse (positive-going) scan. A cyclic voltammogram for 2-bromooctane consists of a single irreversible wave.

Polarographic current maxima along with cyclic voltammetric inverted waves observed for 2-iodooctane are evidence that the mercury cathode is intimately involved in the reduction process. In earlier investigations we have shown that such polarographic and voltammetric phenomena correlate with the probable presence of adsorbed organomercury radicals and with the production of stable diorganomercury compounds during the electrolysis of alkyl halides[1,3,19,20,22] On the other hand, the electrolytic reduction of 2-bromooctane occurs in a region of potentials for which neither polarographic current maxima nor cyclic voltammetric inverted waves are seen; and because no diorganomercury species are obtained from 2-bromooctane, we believe that the mercury electrode does not participate actively in the reduction of this compound.

Our proposition that the electrochemical reduction of 2-iodooctane proceeds in a stepwise fashion—first, to form a radical intermediate and, second, to yield a carbanion—is most strongly supported by the results of pulse polarographic experiments. Pulse polarograms for the reduction of 2-iodooctane exhibit two well-defined steps, just as we have described previously for the reduction of 1-iododecane,[3] and the diffusion currents for the individual waves are virtually identical; the half-wave potentials are −0.94 and −1.47 V in the presence of 0.1 M tetramethylammonium perchlorate and −1.21 and −1.67 V in the presence of 0.1 M tetra-*n*-butylammonium perchlorate. Reduction of 2-bromooctane yields a pulse polarogram showing a single nicely developed wave with a half-wave potential of −1.49 and −1.92 V, respectively, in dimethylformamide containing 0.1 M tetramethylammonium perchlorate and 0.1 M tetra-*n*-butylammonium perchlorate. Significantly, for equal concentrations of 2-bromooctane and 2-iodooctane, the height of the wave for the alkyl bromide is identical with the sum of the heights of the two waves for stepwise reduction of 2-iodooctane, a fact which indicates that 2-bromooctane is reduced essentially directly by uptake of two electrons to form an alkyl carbanion.

Controlled-Potential Electrolyses of 2-Iodooctane and 2-Bromooctane. Compiled in Tables I and II are coulometric data and product distributions obtained at room temperature for controlled-potential electrolyses of 2-iodooctane and 2-bromooctane at mercury in dimethylformamide containing either 0.1 M tetramethylammonium perchlorate or 0.1 M tetra-*n*-butylammonium perchlorate. For all of the experiments, the solvent-supporting electrolyte contained water;[13] but for some of the electrolyses, a proton donor (water or diethyl malonate) was purposely added.

For the reduction of 2-iodooctane at potentials corresponding to the first pulse polarographic wave, the coulometric *n* value is essentially unity, independent of the experimental conditions listed in Table I; moreover, for

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(19) Carroll, W. F., Jr.; Peters, D. G. *J. Org. Chem.* **1978**, *43*, 4633–4637.

(20) Willett, B. C.; Moore, W. M.; Salajegheh, A.; Peters, D. G. *J. Am. Chem. Soc.* **1979**, *101*, 1162–1167.

(21) Fry, A. J.; Krieger, R. L. *J. Org. Chem.* **1976**, *41*, 54–57.

(22) Carroll, W. F., Jr.; Peters, D. G. *J. Am. Chem. Soc.* **1980**, *102*, 4127–4134.

Table II. Coulometric Data and Product Distributions for Controlled-Potential Electrolytic Reduction of 2-Bromooctane at Mercury in Dimethylformamide

		product distribution, %			
conditions[a]	*n* value	octane	1-octene	2-octene	7,8-dimethyltetradecane
(1) 0.1 M Tetramethylammonium Perchlorate					
0.0025 M RBr	1.20	56	16	27	3
0.001 M RBr, 1 M H_2O	1.84	100	1	1	
0.001 M RBr, 0.005 M DEM	1.87	95	1	1	
(2) 0.1 M Tetra-*n*-butylammonium Perchlorate					
0.0025 M RBr	1.21	53	15	30	<1
0.001 M RBr, 1 M H_2O	1.82	86	2	5	
0.001 M RBr, 0.005 M DEM	1.89	98			

[a] RBr = 2-bromooctane, DEM = diethyl malonate.

a given supporting electrolyte, the product distribution does not depend on whether or not a proton donor is introduced into the system. Regardless of the identity of the supporting electrolyte, the yield of octane is comparable to the sum of the yields of 1-octene and 2-octene; in addition, the amount of 1-octene is slightly higher than that of 2-octene. When tetramethylammonium perchlorate serves as the supporting electrolyte, the quantity of di-*sec*-octylmercury is several times larger than that obtained in the presence of tetra-*n*-butylammonium perchlorate. Conversely, the amount of 7,8-dimethyltetradecane is somewhat larger in the presence of tetra-*n*-butylammonium perchlorate than in the presence of tetramethylammonium perchlorate. Thus, the product distribution differs dramatically from that for 1-iodododecane,[1,3] from which only didecylmercury is formed at potentials corresponding to the first pulse polarographic wave.

In the absence of an added proton donor, the coulometric *n* value for reduction of 2-iodooctane at potentials on the second pulse polarographic wave is only slightly larger than at potentials on the first pulse polarographic wave; however, there are significant differences between the product distributions obtained from electrolyses of the alkyl iodide at potentials corresponding to each wave—although the amount of 1-octene is essentially unchanged, the yields of octane and 2-octene are higher and the quantities of di-*sec*-octylmercury and 7,8-dimethyltetradecane are lower at the more negative potentials of the second wave. Deliberate addition of a proton donor (either water or diethyl malonate) to the solvent-supporting electrolyte system has several effects on the electrochemistry of 2-iodooctane at potentials corresponding to the second pulse polarographic wave; the presence of a proton donor raises the coulometric *n* value above 1.7, increases the yield of octane to as high as 90%, causes the quantities of olefins to drop, but (as discussed in more detail below) does not influence the amounts of di-*sec*-octylmercury and 7,8-dimethyltetradecane.

Hydrocarbons are the only products of the electrolysis of 2-bromooctane, regardless of the identity of the supporting electrolyte and regardless of whether reduction is carried out at potentials corresponding to the rising portion of the pulse polarographic wave or at potentials on the plateau of the wave. It is noteworthy that the coulometric *n* value for 2-bromooctane is somewhat larger than that for 2-iodooctane at potentials on the second pulse polarographic wave. For electrolyses of 2-bromooctane with added water or diethyl malonate, the *n* value approaches 2 and octane is almost the only product obtained.

Mechanism for Reduction of 2-Halooctanes. It is convenient to distinguish two modes for the electrolytic reduction of 2-iodooctane. At potentials corresponding to the first pulse polarographic wave, the primary act is one-electron reduction of the starting material to yield the *sec*-octyl radical, whereas at potentials corresponding to the second pulse polarographic wave the starting material undergoes two-electron reduction to form the *sec*-octyl carbanion. In addition, the electrochemical behavior of 2-bromooctane, which parallels that of 2-iodooctane at potentials on the second wave, can be viewed as involving direct production of the carbanion via uptake of two electrons.

Scheme I outlines the reaction pathways that characterize the electrochemical behavior of 2-iodooctane at potentials corresponding to the first pulse polarographic wave. Several pieces of evidence point to the facts that the primary process is one-electron scission of the carbon–iodine bond and that the various electrolysis products are derived from chemical reactions involving the *sec*-octyl radical. First, the coulometric *n* value is unaffected by the addition of a proton donor (either water or diethyl malonate), an observation which indicates the absence of a carbanionic intermediate. Second, the appearance of di-*sec*-octylmercury as a product implies the intermediacy of adsorbed organomercury radicals, the behavior of which has been described in earlier papers.[1,3,12] Third, upon electrolysis of a 2.5 mM solution of 2-iodooctane (75–80% of which was 1,1,1,3,3-pentadeuterio-2-iodooctane) in dimethylformamide containing 0.1 M tetramethylammonium perchlorate at a potential of −1.0 V, 73% of the octane produced was found by means of gas chromatography–mass spectrometry to be 1,1,1,2,3,3-hexadeuteriooctane; this finding is consistent with the proposal that, at potentials on the first pulse polarographic wave, octane (as well as either 1-octene or 2-octene) is formed via disproportionation of the *sec*-octyl radical obtained by one-electron reduction of the starting material.

In the mechanism for the formation of the various products at potentials on the first pulse polarographic wave, an essential initial step is generation of a mercury-stabilized[23] *sec*-octyl radical via one-electron cleavage of the carbon–iodine bond. We believe that production of the mercury-stabilized radical is responsible for stepwise reduction of 2-iodooctane; if the radical were not stabilized, electrolysis of the alkyl iodide would appear as a one-step two-electron process. As shown in Scheme I, the mercury-stabilized *sec*-octyl radical can undergo any of three alternative reactions to yield di-*sec*-octylmercury or 7,8-

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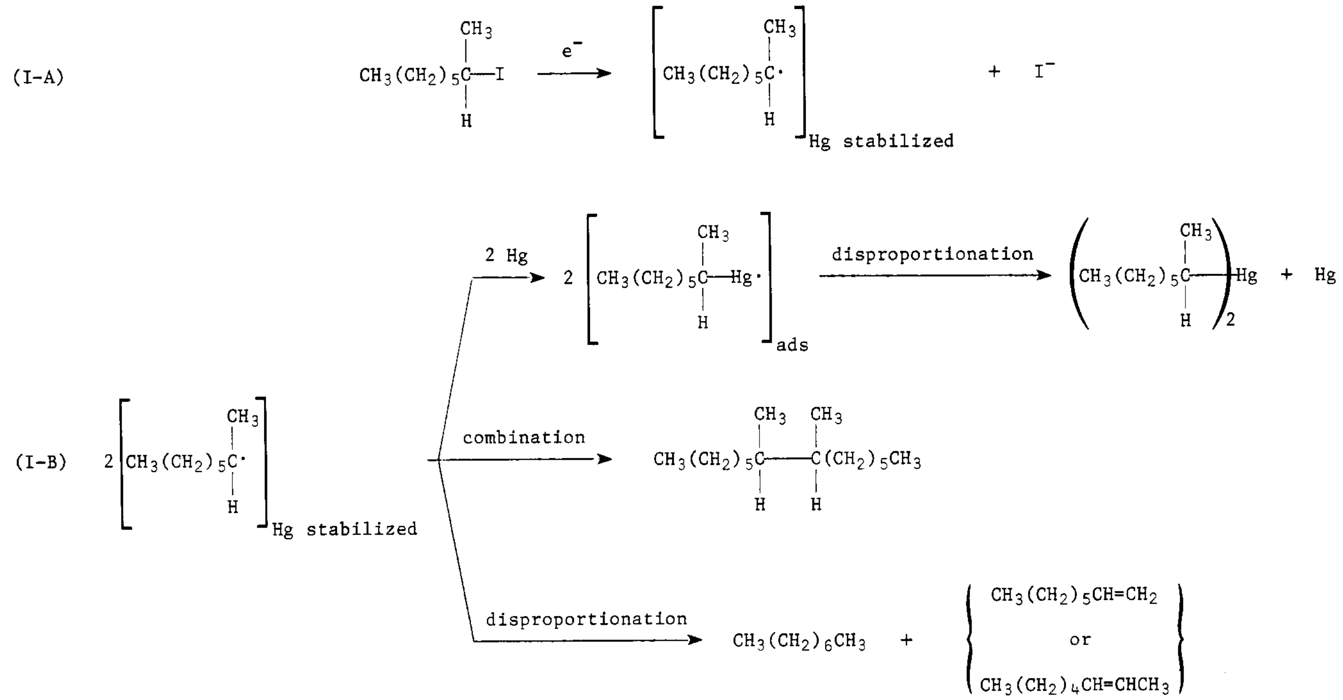
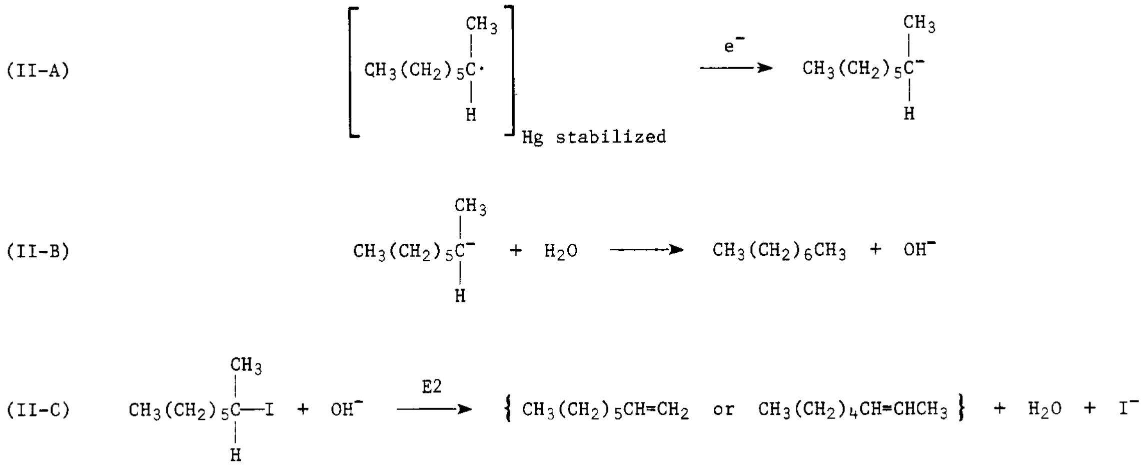
[23] By using the term *mercury-stabilized*, we intend to indicate that the *sec*-octyl radical is in very close proximity to the electrode surface, but we cannot really specify whether the radical is contact adsorbed onto mercury or whether the radical is merely stabilized by being in the double-layer region.

Scheme I[a]



[a] Processes occurring at potentials on the first wave.

Scheme II[a]



[a] Besides processes in Scheme I, the above reactions are proposed to occur at potentials on the second wave.

dimethyltetradecane or octane and octenes.

At potentials corresponding to the second pulse polarographic wave, the behavior of 2-iodooctane resembles that of 1-iodododecane,[3] although the dimeric product (7,8-dimethyltetradecane) formed by electrolysis of the secondary alkyl iodide does not have a counterpart in the reduction of the primary alkyl halide. Scheme II presents the reaction pathways that describe the electrochemistry of 2-iodooctane at potentials on the second wave. We contend that the key intermediate is the *sec*-octyl carbanion; this anion is produced by transfer of one electron to either a mercury-stabilized *sec*-octyl radical or an adsorbed organomercury radical, both of which are derived originally from one-electron reduction of the starting material. Once formed, the carbanion is protonated by water present in the solvent-supporting electrolyte system to yield octane and hydroxide ion. In turn, the hydroxide ion attacks unreduced starting material in an E2 elimination to produce olefins; we found little, if any, of the 2-octanol that would have resulted from the S_N2 reaction between hydroxide and 2-iodooctane. Because the E2 process is highly efficient under the conditions of our experiments, the apparent coulometric n value is close to unity because one molecule of starting material is consumed chemically as another molecule undergoes two-electron reduction. However, as the results listed in Table I reveal, the addition of either water or diethyl malonate to the solvent-supporting electrolyte largely prevents the E2 reaction between hydroxide and unreduced starting material, so that the coulometric n value approaches 2—good evidence that carbanions are produced by electrolytic reduction of 2-iodooctane. Apparently, hydroxide ions are so effectively hydrated in the presence of a high concentration of water that the E2 elimination cannot proceed; on the other hand, hydroxide ions are protonated by diethyl malonate and are thereby not available to attack unreduced 2-iodooctane. It is apparent that diethyl malonate does a much better job than excess water in stopping the E2 process.

Additional proof that the *sec*-octyl carbanion is formed at potentials on the second pulse polarographic wave was afforded by an experiment in which a 2.5 mM solution of 2-iodooctane in dimethylformamide containing 0.1 M tetramethylammonium perchlorate and 1 M D_2O was exhaustively electrolyzed at −1.7 V; we found with the aid of mass spectrometry that 66% of the resulting octane was deuterated in the 2-position, which requires the transfer of a deuterium ion from D_2O to the *sec*-octyl carbanion.

Three observations support the conclusion that, at potentials corresponding to the second pulse polarographic wave, a majority of the olefinic products arise from hydroxide-promoted (E2) dehydrohalogenation of unreduced starting material. First, whereas disproportionation of *sec*-octyl radicals leads to slightly more 1-octene than 2-octene at potentials on the first wave, one expects that an E2 process involving attack of hydroxide (formed from protonation of the *sec*-octyl carbanion by water) on 2-iodooctane will give, as is revealed by the data in Table I, a substantially higher yield of the thermodynamically more stable 2-octene at potentials on the second wave. Second, when a 2.5 mM solution of 2-iodooctane (75–80% of which was 1,1,1,3,3-pentadeuterio-2-iodooctane) in dimethylformamide containing 0.1 M tetramethylammonium perchlorate was electrolyzed at −1.7 V, only 4% of the resulting octane was found to be deuterated in the 2-position, which verifies that processes involving radical intermediates—in the present situation, disproportionation of the pentadeuterio-*sec*-octyl radical to yield 1,1,1,2,3,3-hexadeuteriooctane and olefins—are relatively unimportant. Third, electrolysis of a 2.5 mM solution of 2-iodooctane in dimethylformamide containing 0.1 M tetra-*n*-butylammonium perchlorate and 12.5 mM diethyl malonate at a potential of −1.9 V resulted in the formation of octane (74%), 1-octene (5%), 2-octene (3%), and 7,8-dimethyltetradecane (16%); and the coulometric *n* value was 1.78. Comparison of the latter product distribution with that listed in Table I for reduction of 2-iodooctane in the absence of a proton donor (41% octane, 14% 1-octene, 21% 2-octene, and 17% 7,8-dimethyltetradecane) confirms that E2 elimination is the dominant pathway by which olefins are formed at potentials on the second wave.

Though we consider the *sec*-octyl carbanion to be the dominant intermediate, the appearance of di-*sec*-octylmercury among the products obtained from electrolyses of 2-iodooctane at potentials on the second pulse polarographic wave (Table I) implies that *sec*-octyl radicals are formed along the pathway from starting material to carbanion and that these radicals do result in the formation of the diorganomercury species. Moreover, if reduction of part or all of the alkyl iodide does proceed through the *sec*-octyl radical, it is possible that some of the octane and octenes obtained at potentials on the second wave arise from radical disproportionation, which could never be influenced by the presence or absence of a proton donor; indeed the third set of observations referred to in the preceding paragraph indicates that this may be true.

At potentials on the second wave, what is the origin of 7,8-dimethyltetradecane—S_N2 attack of the *sec*-octyl carbanion on unreduced 2-iodooctane or coupling of a pair of *sec*-octyl radicals? We have found that the yield of dimer depends on the initial concentration of the alkyl iodide; in dimethylformamide containing 0.1 M tetra-*n*-butylammonium perchlorate, electrolysis of 2-iodooctane at a potential of −1.9 V gives 7,8-dimethyltetradecane in yields of 7%, 17%, and 28%, respectively, for 1.0, 2.5, and 12 mM solutions of starting material. However, these data are consistent with either mechanism for the production of 7,8–dimethyltetradecane. More importantly, repeating the second of the preceding three experiments, but with 12.5 mM diethyl malonate added, results in the formation of the dimer in 16% yield; thus, the amount of dimer does not depend on the presence or absence of a proton donor. In addition, electrolysis of a mixture of 2-iodooctane (3 mM) and 2-bromohexane (12 mM) in dimethylformamide containing 0.1 M tetra-*n*-butylammonium perchlorate at a potential of −1.9 V generates 7,8-dimethyltetradecane but neither 5,6-dimethyldecane nor 5,6-dimethyldodecane; although 2-bromohexane undergoes reduction to the alkyl carbanion, the latter species does not attack unreduced 2-iodooctane or 2-bromohexane under the conditions of this experiment. Therefore, we believe that radical coupling is the route by which 7,8-dimethyltetradecane is produced.

For the reduction of 2-iodooctane at potentials corresponding to the first pulse polarographic wave, we have concluded that the olefins arise from disproportionation of *sec*-octyl radicals and that 7,8-dimethyltetradecane is formed by radical coupling. On the other hand, for electrolysis of 2-iodooctane at potentials on the second wave, we contend that olefins are derived mainly from an E2 elimination but that 7,8-dimethyltetradecane still originates from coupling of *sec*-octyl radicals; if radical combination occurs, it seems curious that little radical disproportionation takes place at the most negative potentials. We speculate that a change in the potential of the mercury cathode might cause the ratio of rate constants for radical disproportionation and radical coupling (processes presumably occurring at or near the electrode surface) to vary in a way which enhances significantly the relative extent of radical coupling.

Because reduction of 2-bromooctane occurs at potentials which correspond to the second pulse polarographic wave for 2-iodooctane, the process appears to be a two-electron breakage of the carbon–bromine bond to yield the *sec*-octyl carbanion. Table II shows that the yields of octane and octenes obtained from 2-bromooctane in the absence of a proton donor are nearly identical with those derived from 2-iodooctane under comparable conditions. However, no di-*sec*-octylmercury is produced from the bromo compound; little, if any, 7,8-dimethyltetradecane is formed; and the coulometric *n* value for 2-bromooctane is higher than that for 2-iodooctane. Analogous trends have been seen before in studies of 1-bromodecane and 1-iododecane; we have observed both in the present and in a previous investigation[1] that alkyl bromides display a greater tendency than alkyl iodides to undergo two-electron reduction to an alkyl carbanion at very negative potentials. This tendency is perhaps more strikingly revealed in Table II for those electrolyses done in the presence of water or diethyl malonate; introduction of a proton donor stops the E2 elimination process between hydroxide ion and unreduced 2-bromooctane so well that octane is almost the only electrolysis product and the coulometric *n* value is greater than 1.8. Accordingly, the best representation of the mechanism for the electrolytic reduction of 2-bromooctane entails replacing reaction II-A in Scheme II by a process involving direct transfer of two electrons to the starting material to yield the *sec*-octyl carbanion; then the carbanion undergoes reactions II-B and II-C, the relative importance of each process depending on the availability and source of protons.

Acknowledgment. Appreciation is expressed to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. We are especially grateful to James A. Cleary for his valuable and spirited discussions.

J. Org. Chem. 1982, 47, 3403–3408

Registry No. 2-Iodooctane, 557-36-8; 2-bromooctane, 557-35-7; octane, 111-65-9; 1-octene, 111-66-0; *cis*-2-octene, 7642-04-8; *trans*-2-octene, 13389-42-9; (*d,l*)-7,8-dimethyltetradecane, 82294-06-2; di-*sec*-octylmercury, 82294-07-3; tetramethylammonium perchlorate, 2537-36-2; tetrabutylammonium perchlorate, 1923-70-2; diethyl malonate, 105-53-3; 2-octanol, 123-96-6; 1,1,1,3,3-pentadeuterio-2-iodooctane, 82294-08-4; iodine, 7553-56-2; *sec*-octyl carbanion, 82294-09-5; *meso*-7,8-dimethyltetradecane, 82294-10-8.

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m-Chloroperoxybenzoic Acid Oxidation of *S*-Phenyl 2,2-Dimethylpropanethiosulfinate[1,2]

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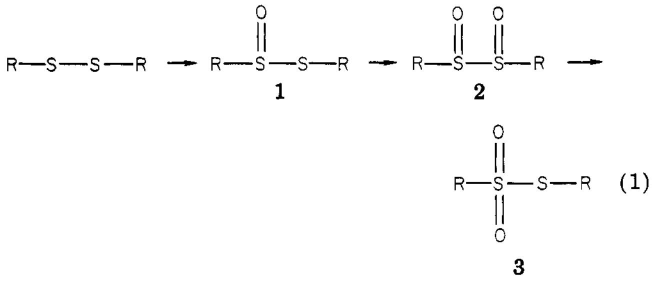
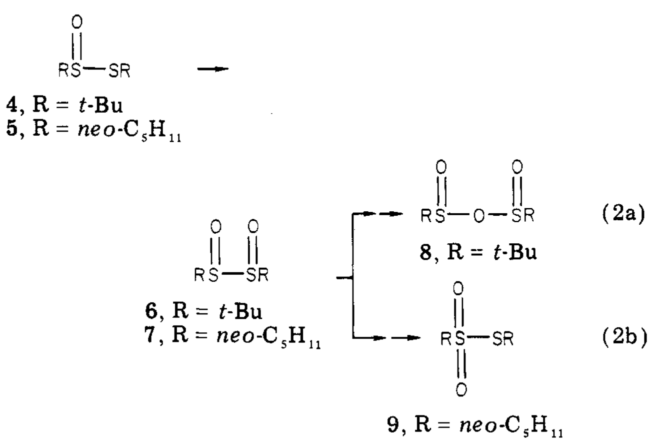
Received November 13, 1981

At −30 °C under nitrogen in $CDCl_3$ the *m*-chloroperoxybenzoic acid (MCPBA) oxidation of *S*-phenyl 2,2-dimethylpropanethiosulfinate (**18**) leads to *S*-(2,2-dimethylpropyl) 2,2-dimethylpropanethiosulfonate (**9**), **18**, *S*-phenyl 2,2-dimethylpropanethiosulfonate (**19**), 2,2-dimethylpropanesulfinic acid (**20**), and 2,2-dimethylpropanesulfonic acid (**21**). These products are consistent with attack by MCPBA at the sulfenyl sulfur atom of **18** to give α-disulfoxides **28** and at the sulfinyl sulfur atom of **18** to give **19**. At 24 °C, **18** reacts with **20** to give **19** and 2,2-dimethylpropanesulfenic acid (**33**), which dimerizes to *S*-(2,2-dimethylpropyl) 2,2-dimethylpropanethiosulfinate (**5**). Possible concerted, ionic, and radical mechanisms for these observations are discussed.

The role of α-disulfoxides (**2**) in the peroxy acid oxidation of disulfides or thiosulfinates (**1**) to thiosulfonates (**3**)[3–24] (eq 1) and in other systems[25–28] is a topic of considerable interest. Diastereomeric α-disulfoxides (**6**, **7**) have been detected via low-temperature ^{1}H NMR and ^{13}C NMR studies of the *m*-chloroperoxybenzoic acid (MCPBA) oxidation of *S*-(2-methyl-2-propyl) 2-methyl-2-propanethiosulfinate (**4**)[3] and *S*-(2,2-dimethylpropyl) 2,2-dimethylpropanethiosulfinate (**5**), respectively[5,7] (eq 2).



$$\mathrm{R{-}S{-}S{-}R} \longrightarrow \underset{\mathbf{1}}{\mathrm{R{-}\overset{\overset{O}{\|}}{S}{-}S{-}R}} \longrightarrow \underset{\mathbf{2}}{\mathrm{R{-}\overset{\overset{O}{\|}}{S}{-}\overset{\overset{O}{\|}}{S}{-}R}} \longrightarrow \underset{\mathbf{3}}{\mathrm{R{-}\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}{-}S{-}R}} \qquad (1)$$



$$\mathrm{R\overset{\overset{O}{\|}}{S}{-}SR} \longrightarrow$$

4, R = *t*-Bu
5, R = *neo*-C_5H_{11}

$$\mathrm{R\overset{\overset{O}{\|}}{S}{-}\overset{\overset{O}{\|}}{S}R} \longrightarrow \mathrm{R\overset{\overset{O}{\|}}{S}{-}O{-}\overset{\overset{O}{\|}}{S}R} \qquad (2a)$$

6, R = *t*-Bu
7, R = *neo*-C_5H_{11}

8, R = *t*-Bu

$$\mathrm{R\overset{\overset{O}{\|}}{S}{-}\overset{\overset{O}{\|}}{S}R} \longrightarrow \mathrm{R\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}{-}SR} \qquad (2b)$$

9, R = *neo*-C_5H_{11}

In symmetrical alkanethiosulfinates (**1**, **4**, **5**), an electrophilic oxidation would be expected to take place preferentially at the electron-rich sulfenyl sulfur atom, while a nucleophilic oxygenation could occur at the electron-poor sulfinyl sulfur atom.[3,5,16–19] However, one cannot unequivocally expect that electrophilic oxidation of an aryl

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(1) Abstracted from the Ph.D. Thesis of C.N.A. University of California, Irvine, CA, 1982.

(2) Presented in part at the Second Chemical Congress of the North American Continent, Las Vegas, NV, Aug. 28, 1980, and the 8th Annual Meeting of NOBCChE, Chicago, IL, Apr 24, 1981.

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