

Electrochemical Reduction of 1-Iododecane and 1-Bromodecane at a Mercury Cathode in Dimethylformamide

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Abstract: Studies of the electrochemical behavior of 1-iododecane and 1-bromodecane at mercury cathodes in dimethylformamide containing tetra-*n*-butylammonium perchlorate or tetramethylammonium perchlorate as supporting electrolyte have shown that reduction of the carbon-halogen bond is a one-electron process. A single polarographic wave is observed for each compound, and a current maximum is seen on the wave for 1-iododecane. Involvement of mercury in the reduction process has been substantiated through isolation of large quantities of didecylmercury from electrolyses of 1-iododecane at potentials positive with respect to the polarographic maximum; little or no organomercury compound is obtained from either starting material at more negative potentials. Other products are decane, 1-decene, and 1-decanol: the decane and 1-decene result from reactions of decyl radicals derived from the one-electron reduction of the carbon-halogen site, and 1-decanol appears to arise from an electrode-assisted displacement of halide by hydroxide ion produced by electrolysis of traces of water in the solvent. Dimethylformamide used as solvent was found to contain *N*-methylformamide as an impurity which, when present, leads to the formation of *N*-decyl-*N*-methylformamide. At negative potentials, telomerization is initiated through addition of radicals, formed from either dimethylformamide or *N*-methylformamide, to 1-decene.

Results of an investigation of the electrolytic reduction of 6-chloro-1-phenyl-1-hexyne at a mercury pool cathode in anhydrous dimethylformamide containing 0.1 M tetra-*n*-butylammonium perchlorate were presented in a recent paper.¹ It was shown that addition of an electron to 6-chloro-1-phenyl-1-hexyne occurs at the carbon-carbon triple bond and initiates isomerization of the starting material to 6-chloro-1-phenyl-1,2-hexadiene as well as a number of intramolecular cyclization reactions. In subsequent studies of 6-iodo-1-phenyl-1-hexyne and 6-bromo-1-phenyl-1-hexyne, for which the carbon-halogen bond and the carbon-carbon triple bond are both reducible (the former more easily than the latter), we experienced difficulty in identifying and accounting for electrolysis products derived from selective reduction of the carbon-halogen bond of each compound. Therefore, to understand the electrochemistry of 6-iodo-1-phenyl-1-hexyne and 6-bromo-1-phenyl-1-hexyne more fully, a detailed examination of the behavior of two simpler species, 1-iododecane and 1-bromodecane, was undertaken.

There have been many publications²⁻¹⁵ dealing with the electrochemical reduction of molecules possessing carbon-halogen bonds, but most of these studies have differed from the present work with respect to the supporting electrolyte-solvent system, the electrode material, or the extent to which the influence of electrolysis potential on the product distribution was investigated. Although reduction of a carbon-halogen bond has been found to be a two-electron process in the majority of earlier papers,²⁻⁸ numerous reports⁹⁻¹⁴ have provided evidence for the one-electron reduction of a carbon-halogen bond and for the formation of organometallic products incorporating the element of which the cathode is composed. For the reduction of 1-iododecane and 1-bromodecane at mercury in dimethylformamide containing either tetra-*n*-butylammonium perchlorate or tetramethylammonium perchlorate as supporting electrolyte, one-electron processes prevail over the entire range of potentials explored. At the least negative potentials employed, only 1-iododecane is electroactive and substantial yields of didecylmercury are obtained. As the potential becomes more negative, both 1-iododecane and 1-bromodecane are reducible, and the distribution of products reveals that other reactions involving radicals predominate—including hydrogen atom abstraction, disproportionation, and telomerization.

Experimental Section

Reagents. Tetra-*n*-butylammonium perchlorate and tetramethylammonium perchlorate, purchased from the G. Frederick Smith Chemical Co., were used without further purification as supporting electrolytes. Dimethylformamide employed as solvent was either Aldrich Spectrophotometric (lot 102547) or Fisher Spectranalyzed (lot 751169) material dried over Linde 4A molecular sieves; gas chromatographic measurements with a 6 ft × 1/8 in. column packed with Porapak Q showed that the water content of such dimethylformamide was approximately 130 ppm. Determination of trace amounts of *N*-methylformamide in the dimethylformamide proved to be of considerable importance in an assessment of the rôle of this impurity in the electrochemical reductions of 1-iododecane and 1-bromodecane. Accordingly, an analysis of the solvent for *N*-methylformamide was accomplished by means of gas chromatography with a 10 ft × 1/8 in. column packed with 15% Carbowax 20M on 80-100 Chromosorb W. Standard-addition experiments revealed the presence of 0.002 and 0.05 mol % *N*-methylformamide, respectively, in the Aldrich and Fisher dimethylformamide. Efforts to decrease the amount of *N*-methylformamide in the dimethylformamide solvent by means of distillation over calcium hydride resulted in an impurity level no less than approximately 0.001 mol %.

Commercially available 1-iododecane (Chemical Samples Co., 95%) and 1-bromodecane (J. T. Baker, 97%) were purified by means of vacuum distillation; the fraction of 1-iododecane boiling at 95-96 °C (1.2 mm) and the fraction of 1-bromodecane boiling at 81-82 °C (1.4 mm) were utilized for electrochemical experiments. Both fractions were determined with the aid of gas chromatography to be at least 99% pure.

Instrumentation and Procedures. Descriptions of the electrolysis cell, the instrumentation for polarography and controlled-potential coulometry, and the procedures for electrochemical experiments and product analyses have been published previously.^{1,16} 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;¹⁷ this electrode has a potential of -0.750 V vs. the aqueous saturated calomel electrode.

Gas chromatographic analyses were performed with a Hewlett-Packard Model 5700A dual-column instrument equipped with a thermal conductivity detector; columns used included the previously mentioned Carbowax column, a 10 ft × 1/8 in. column and a 20 in. × 1/8 in. column both packed with 10% OV-101 on 80-100 Gas Chrom P, and a 20 in. × 1/8 in. column packed with 10% UC W98 on 80-100 Chromosorb W. In addition, the chromatograph was modified for preparative-scale work in a manner reported elsewhere;¹ a 16 in. ×

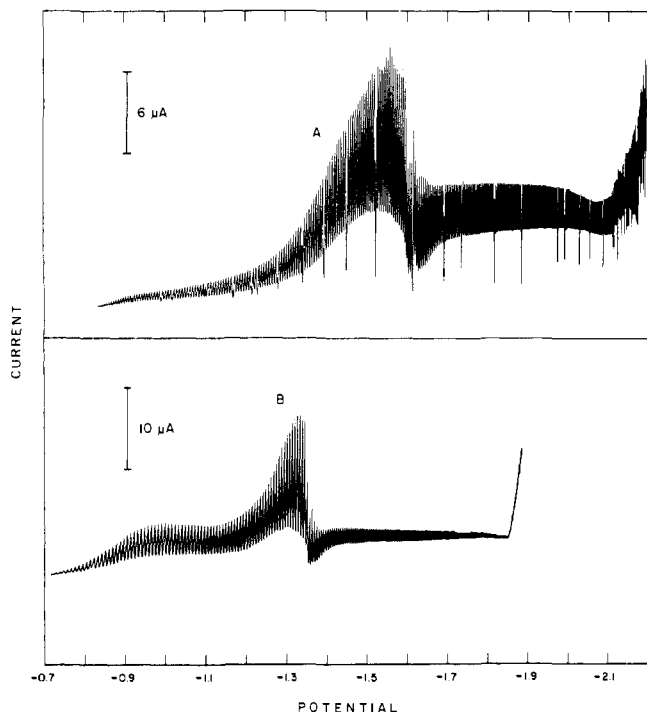


Figure 1. (A) Polarogram for a 0.0025 M solution of 1-iododecane in dimethylformamide containing 0.1 M tetra-*n*-butylammonium perchlorate. (B) Polarogram for a 0.0025 M solution of 1-iododecane in dimethylformamide containing 0.1 M tetramethylammonium perchlorate.

$\frac{1}{4}$ in. column packed with 10% SE-30 on 80-100 Chromosorb W was utilized for the preparative-scale chromatography.

A Varian EM-360 spectrometer was employed to record NMR spectra, and all chemical shifts are reported in ppm downfield from tetramethylsilane. Mass spectrometric data for *N*-decyl-*N*-methylformamide and didecylmercury were obtained with a Varian CH-7 spectrometer which, when coupled to a Varian Aerograph Series 1200 gas chromatograph through a Llewellyn separator, permitted mass spectra for individual telomeric electrolysis products to be recorded. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory (Woodside, N.Y.) and by Midwest Microlab, Ltd. (Indianapolis, Ind.).

Before every electrolysis, an electroinactive internal standard (phenylcyclohexane) was added to the sample solution, and an experimentally measured gas chromatographic sensitivity factor for each electrolysis product (except the telomers for which the sensitivity factors were assumed to be unity) was utilized to determine the recovery of that compound. All product yields are absolute and are expressed in terms of the percentage of starting material incorporated into the particular species.

Product Identification. Among the electrolysis products, decane, 1-decene, and 1-decanol were identified by comparison of their gas chromatographic retention times with those of commercially available authentic samples.

N-Decyl-*N*-methylformamide, obtained pure from electrolyzed solutions by means of preparative-scale gas chromatography, gave the following spectral data: NMR (CDCl_3) δ 8.1 (s, 1, formyl H), 3.2 (m, 2, CH_2N), 2.8 (m, 3, CH_3N), 1.2 (m, 16, CH_2), and 0.9 (t, 3, CH_3). Mass spectra at 70 eV yielded the following results, relative abundances being reported in parentheses: m/e 199, M^+ (1%); 198, $\text{M}^+ - \text{H}$ (2.1%); 72, $\text{M}^+ - \text{C}_9\text{H}_{19}$ (100%). Anal. Calcd for $\text{C}_{12}\text{H}_{25}\text{NO}$: C, 72.31; H, 12.64; N, 7.03; O, 8.02. Found: C, 72.47; H, 11.89; N, 6.39. To confirm the identity of *N*-decyl-*N*-methylformamide as an electrolysis product, it was synthesized independently. To 10 g of decanoic acid was added 5 mL of thionyl chloride, and the mixture was refluxed for approximately 2 h. After removal of the excess thionyl chloride through vacuum distillation, the acid chloride was cooled and added to an excess of a 40% solution of methylamine in water. A vigorous reaction occurred, yielding *N*-methyldecanamide. This product was dissolved in diethyl ether, the solution was added dropwise to 2 g of lithium aluminum hydride in ether, and the mixture was refluxed for several hours. Decylmethyl-

amine, the resulting product, was added dropwise to a formic acid-acetic anhydride mixture, after which the 55% yield of *N*-decyl-*N*-methylformamide was isolated pure by means of column chromatography; we used a 25 cm \times 1.7 cm column packed with silica gel and eluted first with diethyl ether to remove extraneous species and then with methanol to collect the *N*-decyl-*N*-methylformamide. Both the gas chromatographic retention time and the NMR spectrum of the prepared *N*-decyl-*N*-methylformamide were identical with those of the electrolysis product.

Didecylmercury was isolated pure from electrolyzed solutions by means of gel-permeation chromatography with a 30 cm \times 2.5 cm column containing Bio-Beads S-X8 (Bio-Rad Laboratories); benzene was employed as the mobile phase. A 20-eV mass spectrum of the recovered material exhibited the characteristic isotope pattern of mercury. Anal. Calcd for $\text{C}_{20}\text{H}_{42}\text{Hg}$: C, 49.72; H, 8.76; Hg, 41.52. Found: C, 49.89; H, 8.81; Hg, 41.24.

Telomers were detected as products when concentrated extracts of electrolyzed solutions were analyzed chromatographically with a 20 in. \times $\frac{1}{8}$ in. column containing 10% OV-101 on 80-100 Gas Chrom P. Several sets of chromatographic peaks were resolved which, when characterized by means of gas chromatography-mass spectrometry, yielded parent peaks having m/e 311, 325, 451, 465, and 479. Suspecting that these compounds were telomers formed by reaction of 1-decene with free radicals derived from either dimethylformamide or *N*-methylformamide, we synthesized such telomers independently according to procedures previously reported^{18,19} by treating 1-decene in the presence of di-*tert*-butyl peroxide at 140 °C with dimethylformamide, *N*-methylformamide, dimethylamine, or methylamine. By comparing gas chromatographic and mass spectrometric data for the suspected telomeric electrolysis products with similar information for the various chemically prepared telomers, we conclude that the compounds with molecular weights of 311, 325, 451, 465, and 479 correspond to substances having formulas $\text{C}_{21}\text{H}_{45}\text{N}$, $\text{C}_{22}\text{H}_{47}\text{N}$, $\text{C}_{31}\text{H}_{65}\text{N}$, $\text{C}_{32}\text{H}_{67}\text{N}$, and $\text{C}_{32}\text{H}_{65}\text{NO}$, respectively.

Results and Discussion

Polarographic Behavior of 1-Iododecane and 1-Bromodecane. Figure 1A shows a polarogram for a 0.0025 M solution of 1-iododecane in dimethylformamide containing 0.1 M tetra-*n*-butylammonium perchlorate as supporting electrolyte. An obvious feature of the polarogram is the enormous maximum which peaks at -1.56 V. Following the maximum, a small current minimum is observed at approximately -1.62 V, and recovery to a normal diffusion-controlled current plateau due to reduction of the carbon-iodine bond is almost complete at -1.75 V. Measurement of the half-wave potential for reduction of 1-iododecane is rendered impossible by the large maximum. In contrast, a polarogram for 0.0025 M 1-bromodecane in the same supporting electrolyte-solvent exhibits no current maximum, and the half-wave potential for reduction of the carbon-bromine bond is -1.81 V.

A polarogram for a 0.0025 M solution of 1-iododecane in dimethylformamide containing 0.1 M tetramethylammonium perchlorate is seen in Figure 1B. Compared with the behavior observed when tetra-*n*-butylammonium perchlorate is employed as supporting electrolyte, the maximum is shifted somewhat more than 200 mV and the polarographic wave for reduction of the carbon-iodine bond is moved at least 400 mV, both toward more positive potentials. Thus, the polarogram for 1-iododecane in the presence of tetramethylammonium perchlorate has a readily measurable half-wave potential of -0.86 V and exhibits a well-defined limiting current plateau in the middle of which appears a prominent maximum. For the reduction of 1-bromodecane in dimethylformamide containing 0.1 M tetramethylammonium perchlorate, the half-wave potential for reduction of the carbon-bromine bond is shifted to -1.40 V and no maximum is observed on the polarogram. Shifts in half-wave potentials for the reduction of alkyl halides arising from the use of different tetraalkylammonium salts as supporting electrolytes have been noted previously,^{20,21} but the possible effects of such behavior on the distribution of products

Table I. Coulometric Data and Product Distributions for Electrolytic Reduction of 0.0025 M 1-Iododecane and 1-Bromodecane in Dimethylformamide Containing 0.1 M Tetra-*n*-butylammonium Perchlorate and 0.05% *N*-Methylformamide

Potential, V	Compound	<i>n</i> value	Product distribution, %				
			Decane	1-Decene	1-Decanol	<i>N</i> -Decyl- <i>N</i> -methylformamide	Didecylmercury
-1.1	1-Iododecane	0.89	1		1		100
-1.3	1-Iododecane	0.88	4		4		96
-1.4	1-Iododecane	0.83	12	1	4	8	78
-1.5	1-Iododecane	0.90	21	3	4	11	64
-1.6	1-Iododecane	0.86	36	7	9	25	10
-1.7	1-Iododecane	0.90	42	6	5	28	9
-1.9	1-Iododecane	0.75	44	3	9	40	
-1.9	1-Bromodecane	1.03	44	3	3	37	

obtained from large-scale controlled-potential electrolyses have not been fully documented.

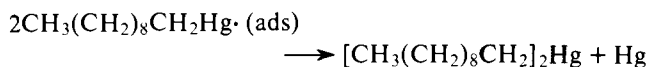
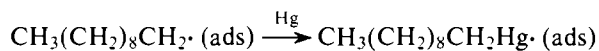
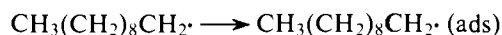
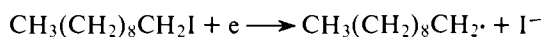
We have observed a strong correlation between the appearance of a polarographic maximum for reduction of an organic halide and the possible formation of substantial amounts of diorganomercury electrolysis products. This is true for 1-iododecane, as described subsequently in this paper, and for 6-iodo-1-phenyl-1-hexyne, 6-bromo-1-phenyl-1-hexyne, 5-iodo-1-phenyl-1-pentyne, 5-bromo-1-phenyl-1-pentyne, and 1-iodo-5-decyne, all of which are now being examined in our laboratory. In addition, cyclic voltammograms for each of the preceding compounds exhibit an inverted wave^{22,23} on the anodic sweep which appears to be the voltammetric analogue of the polarographic maximum. Compounds such as alkyl chlorides, acetylenic chlorides, and simple alkyl bromides, which show neither a polarographic maximum nor an inverted voltammetric wave, yield little or no diorganomercury products upon large-scale electrolytic reduction. In the work with 1-iododecane, electrolyses done at potentials positive with respect to the polarographic maximum give large quantities of didecylmercury, whereas much smaller amounts of the diorganomercury product result from electrolyses at potentials more negative than the maximum. Conceivably, the polarographic maximum signals desorption of organic radicals from the surface of the mercury cathode, a process which would greatly diminish the formation of organomercury radicals and the appearance of diorganomercury electrolysis products.

Although a variation in the trace amount of *N*-methylformamide found in dimethylformamide influences considerably the distribution of products resulting from controlled-potential electrolyses, polarograms for 1-iododecane and 1-bromodecane are not affected by the presence of this impurity.

Controlled-Potential Electrolyses of 1-Iododecane and 1-Bromodecane in Dimethylformamide Containing 0.05% *N*-Methylformamide. Listed in Table I are the coulometric results and product distributions for controlled-potential electrolyses of 1-iododecane and 1-bromodecane at mercury pool cathodes in dimethylformamide containing 0.1 M tetra-*n*-butylammonium perchlorate and 0.05% *N*-methylformamide. Normal exponential current-time curves were observed in all experiments. Over the entire range of potentials employed for the electrolysis of 1-iododecane, there is no significant deviation from a coulometric *n* value of unity, indicating that the net process is the one-electron reduction of the carbon-halogen bond. Actually, the reported *n* values are less than unity because small aliquots of the sample solutions were removed for mercury analysis at intervals during the electrolyses.²⁴ In addition, formation of 1-decanol is believed not to be an electron-consuming process; further information about the reaction involved in the production of 1-decanol will be presented later.

Though not indicated in Table I, the use of tetramethylammonium perchlorate in several experiments revealed that the *n* value is not dependent on the identity of the supporting electrolyte.

At the most positive potential (-1.1 V) utilized to reduce 1-iododecane, an essentially quantitative amount of didecylmercury is obtained; and, for all potentials positive with respect to the polarographic maximum seen in Figure 1A, the percentage of the diorganomercury compound remains relatively high. For potentials more negative than the polarographic maximum, the yield of didecylmercury falls very abruptly. Electrolytic reduction of a 0.0025 M solution of 1-bromodecane, which does not exhibit a polarographic maximum, results in no detectable formation of didecylmercury. When tetramethylammonium perchlorate is employed as supporting electrolyte for the reduction of 1-iododecane, the rapid decrease in the quantity of didecylmercury occurs between -1.3 and -1.4 V, the region of the polarographic maximum in Figure 1B. We believe that adsorbed decyl radicals are essential for the production of didecylmercury and that the following mechanistic scheme could be operative at potentials more positive than the polarographic maximum:²⁵



At potentials negative with respect to the polarographic maximum, the absence of adsorbed decyl radicals minimizes the formation of didecylmercury. Instead, the decyl radicals are free to undergo reactions leading to other electrolysis products. Once formed, didecylmercury is not electroactive.

That the coulometric *n* value is close to unity and that no Hofmann elimination products (tri-*n*-butylamine and 1-butene) derived from deprotonation of the tetra-*n*-butylammonium cation were detected are strong pieces of evidence for the formation of decane and 1-decene by pathways involving radicals not carbanions. Accordingly, we propose that most of the decane arises through transfer of a hydrogen atom to the decyl radical. Conceivably, the decyl radical abstracts a hydrogen atom from *N*-methylformamide

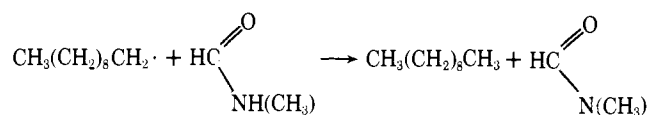
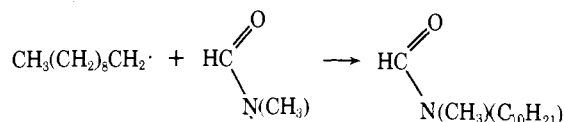


Table II. Coulometric Data and Product Distributions for Electrolytic Reduction of 0.0025 M 1-Iododecane and 1-Bromodecane in Dimethylformamide Containing 0.002% *N*-Methylformamide

Potential, V	Compound	<i>n</i> value	Product distribution, %				
			Decane	1-Decene	1-Decanol	<i>N</i> -Decyl- <i>N</i> -methylformamide	Didecylmercury
(a) 0.1 M Tetra- <i>n</i> -butylammonium Perchlorate as Supporting Electrolyte							
-1.1	1-Iododecane	0.87	2		3	1	99
-1.3	1-Iododecane	0.93	5		1		96
-1.5	1-Iododecane	1.09	19	6	2	4	55
-1.7	1-Iododecane		39	14	4	3	5
-1.8	1-Iododecane	1.05	43	14	3	4	5
-1.7	1-Bromodecane	0.82	51	20	1	2	
-1.8	1-Bromodecane	1.00	52	19	2	6	
-1.9	1-Bromodecane	1.04	53	21	2	3	
(b) 0.1 M Tetramethylammonium Perchlorate as Supporting Electrolyte							
-1.0	1-Iododecane		1		1		99
-1.4	1-Iododecane	0.94	42	20	2	2	6
-1.7	1-Iododecane	1.04	47	28	2	3	
-1.7	1-Bromodecane		51	23	1	3	

and combination of the radical derived from *N*-methylformamide with another decyl radical could result in the formation of *N*-decyl-*N*-methylformamide:



An alternate mechanism for production of decane and *N*-decyl-*N*-methylformamide involves alkylation of the oxygen atom of *N*-methylformamide by decyl halide, followed by loss of a proton to yield the imino ether;²⁶ in turn, the proton could be reduced to a hydrogen atom which couples with a decyl radical to form decane, and the imino ether could undergo a Lander rearrangement to give *N*-decyl-*N*-methylformamide.²⁷ Further work is underway in an effort to determine the correct mechanism.²⁸ Coupling of decyl radicals appears to be of minor significance; no measurable yield of the expected dimer, eicosane, was obtained at any electrolysis potential. On the other hand, we believe that disproportionation of decyl radicals to yield decane and 1-decene is the only important source of the olefin. As the data in Table I reveal, the overall yield of 1-decene is much smaller than that of decane. Thus, in the presence of 0.05% *N*-methylformamide, disproportionation of decyl radicals is relatively unimportant.

For electrolyses of 1-iododecane and 1-bromodecane at potentials more negative than the polarographic maximum for 1-iododecane, the product yields listed in Table I do not total 100%. In the final section of this paper, it will be demonstrated that the remaining products are telomers resulting from addition to 1-decene of radicals derived from both dimethylformamide and *N*-methylformamide.

Controlled-Potential Electrolyses of 1-Iododecane and 1-Bromodecane in Dimethylformamide Containing 0.002% *N*-Methylformamide. Product distributions for electrolyses of 1-iododecane and 1-bromodecane in dimethylformamide containing only 0.002% *N*-methylformamide are shown in Table II. Measurements of *n* values indicate that reduction of the carbon-halogen bond for each compound is a net one-electron process throughout the range of potentials investigated. For the electrolysis of 1-iododecane at potentials positive with respect to the polarographic maximum in the presence of either tetra-*n*-butylammonium perchlorate or tetramethylammonium perchlorate, the distribution of products is quite similar to that reported in the preceding section, didecylmer-

cury being the major species formed. Although the yield of decane obtained upon reduction of 1-iododecane at each potential given in Tables I and II is not affected much by a variation in the quantity of *N*-methylformamide impurity in the solvent, it appears that the principal pathway for production of decane is controlled by the amount of *N*-methylformamide. In the presence of 0.002% *N*-methylformamide, disproportionation of decyl radicals to form decane and 1-decene is a more important process. Evidently, when only a small quantity of *N*-methylformamide is present in the dimethylformamide, there is little opportunity for transfer of a hydrogen atom from *N*-methylformamide to the decyl radical; consequently, there is less chance for combination of $\text{C}_{10}\text{H}_{21}\cdot$ and $\text{HCON}(\text{CH}_3)\cdot$ radicals to form *N*-decyl-*N*-methylformamide. For formation of decane and *N*-decyl-*N*-methylformamide via the route which proceeds through an imino ether, a low concentration of the *N*-methylformamide impurity greatly diminishes the probability of the initial reaction between *N*-methylformamide and the decyl halide. With 0.05% *N*-methylformamide, either of the preceding reactions which involve this impurity and which lead to the production of decane takes precedence over disproportionation of decyl radicals.

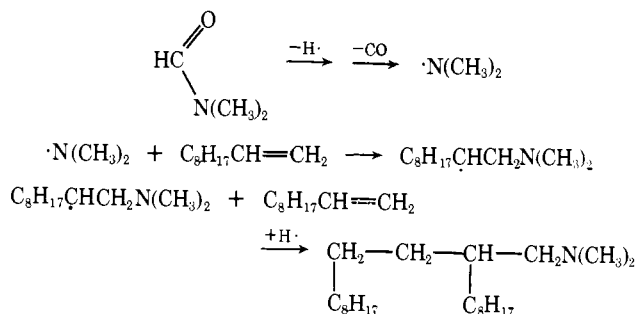
There is one notable difference between the product distributions presented in Table II for 1-iododecane and 1-bromodecane. For the latter compound, the yields of decane and 1-decene tend to be slightly higher, but as yet no obvious explanation for this behavior has emerged from our work.

As stated earlier, 1-decanol arises presumably via the $\text{S}_{\text{N}}2$ reaction between hydroxide ion and either 1-iododecane or 1-bromodecane. Hydroxide ion results from the reduction of unavoidable traces of water in dimethylformamide during preelectrolysis of the supporting electrolyte-solvent system. Fluctuations in the amount of water present in the solvent from one electrolysis to another cause the yields of 1-decanol reported in both Tables I and II to vary. Insight into the mechanism responsible for the formation of 1-decanol was obtained from a set of experiments carried out with dimethylformamide containing 0.1 M tetra-*n*-butylammonium perchlorate and 0.002% *N*-methylformamide as well as an added amount of water 30 times larger than that in all other electrolyses. In a typical experiment, a 60-min preelectrolysis of the supporting electrolyte-solvent was performed at -2.0 V, during which the water was reduced to hydroxide ions and molecular hydrogen; 1-iododecane (0.0025 M) and internal standard (phenylcyclohexane) were syringed into the cell. Then, without the

passage of any current, the solution was stirred over the mercury pool cathode for 2 h, a small aliquot was withdrawn, and the solution remaining in the cell was exhaustively electrolyzed at -1.9 V for 70 min; upon correction for starting material lost through removal of the aliquot, the n value for this experiment was less than that found when no extra water was introduced. Gas chromatographic analysis revealed the presence of only 0.5% 1-decanol in the aliquot, whereas approximately 15% 1-decanol was found in the solution after the exhaustive electrolysis. On the basis of these observations, we conclude that 1-decanol is not formed merely via a simple, homogeneous S_N2 reaction between hydroxide ion and 1-iododecane. Instead, it appears that the carbon-iodine bond of 1-iododecane experiences a heterogeneous, electrode-assisted ionization which facilitates attack by hydroxide ion to yield the alcohol.

At negative electrolysis potentials, the products listed in Tables I and II do not account for all the starting material. However, gas chromatograms for highly concentrated extracts of electrolyzed solutions revealed the presence of at least ten species with relatively high molecular weights believed to be telomers formed by the reaction of 1-decene with radicals derived from either *N*-methylformamide or dimethylformamide. These substances were impossible to detect under conditions utilized for routine product analysis, because no one compound gives a chromatographic peak with a height greater than 1% of the peak height for the internal standard (phenylcyclohexane). Likely telomeric products were synthesized independently, as outlined earlier, and their gas chromatographic and mass spectrometric characteristics were compared with those of the electrolysis products. Among a substantial list of possibilities, the characterized telomers fall into two categories, namely, formamides derived from *N*-methylformamide and amines derived from the decarbonylation of *N*-methylformamide or dimethylformamide; no amides derived from either *N*-methylformamide or dimethylformamide were found. Five telomeric electrolysis products have been identified with reasonable certainty. First is $C_{22}H_{47}N$, a 2:1 telomer incorporating two molecules of 1-decene and a dimethylamino radical, which could be formed according to Scheme I.²⁹ Also found as a 2:1 telomer was $C_{21}H_{45}N$, which

Scheme I



consists of two molecules of 1-decene and a methylamino radical derived from *N*-methylformamide in a manner similar to that of the preceding sequence of reactions.³⁰ Finally, a set of three 3:1 telomers was identified, including $C_{31}H_{65}N$ (composed of 1-decene and a methylamino radical), $C_{32}H_{67}N$ (derived from 1-decene and a dimethylamino radical), and $C_{32}H_{65}NO$ (formed from 1-decene and either a $\text{HCON}(\text{CH}_3)$ or $\text{HCONHCH}_2\cdot$ radical). In addition to these materials, the unidentified substances are believed to be other 2:1 and 3:1 telomers, because their retention times are similar to those of the above five species; furthermore, minute quantities of

compounds thought to be 4:1 telomers were seen chromatographically. When the amount of starting material incorporated into each telomer is included in calculations of the total product recovery, it is possible to account for more than 90% of the original alkyl halide.

Acknowledgments. Appreciation is expressed to the National Science Foundation for financial support of this research through Grant GP-36568; to the National Science Foundation for Grant GP-32225 which provided the mass spectrometer-computer system; to David Peterson for assistance with the use of the gas chromatograph-mass spectrometer facilities; and to William F. Carroll, Jr., for many helpful discussions.

References and Notes

- (1) W. M. Moore, A. Salajegheh, and D. G. Peters, *J. Am. Chem. Soc.*, **97**, 4954 (1975).
- (2) P. J. Elving, I. Rosenthal, and M. K. Kramer, *J. Am. Chem. Soc.*, **73**, 1717 (1951).
- (3) P. J. Elving and R. E. Van Atta, *J. Electrochem. Soc.*, **103**, 676 (1956).
- (4) F. L. Lambert and K. Kobayashi, *J. Am. Chem. Soc.*, **82**, 5324 (1960).
- (5) J. Závada, J. Krupička, and J. Slicher, *Collect. Czech. Chem. Commun.*, **28**, 1664 (1963).
- (6) J. W. Sease, P. Chang, and J. L. Groth, *J. Am. Chem. Soc.*, **86**, 3154 (1964).
- (7) J. A. Dougherty and A. J. Diefenderfer, *J. Electroanal. Chem.*, **21**, 531 (1969).
- (8) M. R. Rifi, *Tetrahedron Lett.*, 1043 (1969).
- (9) M. Fleischmann, D. Pletcher, and C. J. Vance, *J. Electroanal. Chem.*, **29**, 325 (1971).
- (10) M. Fleischmann, G. Mengoli, and D. Pletcher, *Electrochim. Acta*, **18**, 231 (1973).
- (11) O. R. Brown and K. Taylor, *J. Electroanal. Chem.*, **50**, 211 (1974).
- (12) J. Casanova and H. R. Rogers, *J. Am. Chem. Soc.*, **96**, 1942 (1974).
- (13) K. B. Wiberg and G. A. Epling, *Tetrahedron Lett.*, 1119 (1974).
- (14) F. L. Lambert and G. B. Ingall, *Tetrahedron Lett.*, 3231 (1974).
- (15) Comprehensive reviews and bibliographies concerning electrochemical reduction of organic halogen compounds can be found in the following books: (a) M. M. Baizer, Ed., "Organic Electrochemistry", Marcel Dekker, New York, N.Y., 1973, pp 279-314; (b) A. J. Fry, "Synthetic Organic Electrochemistry", Harper & Row, New York, N.Y., 1972, pp 169-187; (c) C. K. Mann and K. K. Barnes, "Electrochemical Reactions in Nonaqueous Systems", Marcel Dekker, New York, N.Y., 1970, pp 201-244.
- (16) W. M. Moore and D. G. Peters, *J. Am. Chem. Soc.*, **97**, 139 (1975).
- (17) L. W. Marple, *Anal. Chem.*, **39**, 844 (1967).
- (18) W. H. Urry and O. O. Juveland, *J. Am. Chem. Soc.*, **80**, 3322 (1958).
- (19) L. Friedman and H. Shechter, *Tetrahedron Lett.*, 238 (1961).
- (20) K. P. Butin, N. A. Belokoneva, A. A. Zenkin, I. P. Beletskaya, and O. A. Reutov, *Dokl. Akad. Nauk SSSR*, **211**, 878 (1973).
- (21) A. J. Fry and R. L. Krieger, *J. Org. Chem.*, **41**, 54 (1976).
- (22) B. Fleet and R. D. Jee, *J. Electroanal. Chem.*, **25**, 397 (1970).
- (23) D. A. Tyssee, *J. Electroanal. Chem.*, **30**(3), App. 14-16 (1971).
- (24) Originally, we intended to analyze these aliquots for mercury by means of atomic absorption spectrophotometry; however, when gas chromatography proved to be suitable for the direct determination of didecylmercury, the former approach was abandoned.
- (25) No conclusive evidence has been obtained to rule out the alternate mechanism in which 1-iododecane is adsorbed before the electron-transfer step occurs and in which the adsorbed alkyl iodide is reduced directly to an adsorbed decyl radical that then interacts with the electrode material to form didecylmercury.
- (26) R. Gompper and O. Christmann, *Chem. Ber.*, **92**, 1935 (1959).
- (27) M. Goffier and R. Milcent, *Tetrahedron Lett.*, 3871 (1974).
- (28) Another pathway for the formation of *N*-decyl-*N*-methylformamide is attack of the *N*-methylformamide radical upon 1-decene, followed by hydrogen atom abstraction. This mechanism has been ruled out by large-scale electrolyses in which 1-decene was added prior to reduction of either 1-iododecane or 1-bromodecane. In these experiments, there was no change in the yield of *N*-decyl-*N*-methylformamide. However, this does not exclude the possibility that the *N*-methylformamide radical attacks 1-decene to form higher telomers.
- (29) We believe that the initiator radical must come from *N*-methylformamide or dimethylformamide and that this radical attacks 1-decene to form a more stable secondary radical. We propose that the secondary radical, in turn, reacts with another molecule of 1-decene instead of a decyl radical, because coupling of two carbon radicals appears not to be an important process (as evidenced by the absence of eicosane among the electrolysis products). Abstraction of a hydrogen atom by the growing chain ends the telomerization apparently after incorporation of no more than four molecules of 1-decene.
- (30) That abstraction of the hydrogen atom attached to the carbonyl group of dimethylformamide or *N*-methylformamide (followed by rapid decarbonylation) does occur is evidenced by the appearance of telomers containing the dimethylamino and methylamino moieties, respectively.