Radicals and Carbanions as Intermediates in the Electrochemical Reduction of 1-Iododecane at Mercury. Effect of Potential, Electrolysis Time, and Water Concentration on the Mechanism

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Abstract: Polarograms for 1-iododecane in dimethylformamide containing 0.1 F tetramethylammonium perchlorate and 0.050 M water exhibit two waves, with a prominent maximum appearing on the rising portion of the second wave. At potentials positive with respect to the maximum, 1-iododecane undergoes one-electron reduction to yield decyl radicals which become adsorbed onto the mercury cathode; two adsorbed decylmercury radicals interact to give didecylmercury, the only electrolysis product obtained in this potential region. At potentials negative of the maximum, chronocoulometry, cyclic voltammetry, and pulse polarography have revealed that reduction of 1-iododecane on a short time scale is a two-electron process; however, when 1-iododecane is subjected to comparatively slow controlled-potential electrolysis at these potentials, the coulometric *n* value is unity. Experiments done with deuterium-labeled trapping agents have confirmed that the decyl carbanion is the predominant intermediate at potentials negative of the maximum, although some decyl radicals are formed. At potentials negative of the maximum, the water content of the supporting electrolyte-solvent system as well as the electrolysis time greatly influences the reduction of 1-iododecane. In the presence of 0.050 M water, electrolytically generated decyl carbanions are protonated by water to yield hydroxide ion and decane, the hydroxide attacks unreduced alkyl iodide to give 1-decene and 1-decanol via E2 and S_N2 reactions, respectively, and the apparent *n* value is close to unity. When the concentration of water is low, decyl carbanions are probably protonated by dimethylformamide, little 1-decene and 1-decanol are produced, and the *n* value approaches two.

In a recent communication[1] we presented results showing that the number of electrons involved in the electrochemical reduction of 1-iododecane at mercury in dimethylformamide containing tetramethylammonium perchlorate depends on the time scale[2] of the electrolysis as well as on the potential of the cathode. Furthermore, preliminary evidence was offered to indicate that the water content of the supporting electrolyte-solvent system plays a crucial role in the pathway for reduction of the primary alkyl iodide.

Polarograms for 1-iododecane in dimethylformamide containing 0.1 F tetramethylammonium perchlorate and approximately 0.050 M water exhibit two waves. Diffusion-current measurements have established that the first wave is attributable to one-electron reduction of the carbon–halogen bond. On the rising portion of the second polarographic wave is an anomalous and prominent maximum, after which the limiting current returns to a level corresponding to an overall *n* value between one and two. Thus, at potentials positive with respect to the polarographic maximum, 1-iododecane presumably undergoes reduction to yield a decyl radical; but, at potentials more negative than the polarographic maximum, the alkyl iodide appears to be reduced to a mixture of radical and carbanionic intermediates.

On the basis of both previous studies[1,3] and the present investigation, we have concluded that, at potentials positive of the polarographic maximum in dimethylformamide containing tetramethylammonium perchlorate, decyl radicals formed by one-electron reduction of 1-iododecane are adsorbed onto the mercury electrode and that the resulting decylmercury radicals lead quantitatively to didecylmercury.

With regard to processes occurring at potentials more negative than the polarographic maximum, the picture has heretofore been less clear. In an earlier paper[3] dealing with the electrochemistry of 1-iododecane in dimethylformamide containing tetraalkylammonium salts, the products formed in controlled-potential electrolyses at mercury pool cathodes were determined and the coulometric *n* value for reduction of the carbon–iodine bond was found to be unity at potentials

negative with respect to the polarographic maximum; these findings led us to propose that the principal electrolysis products (decane and 1-decene) arise from a radical intermediate. In a study of the behavior of 1-bromobutane, which can be electrolyzed only at a potential more negative than the polarographic maximum for 1-iododecane, Wagenknecht[4] observed that reduction of the carbon–bromine bond is a one-electron reaction involving a butylmercury radical in dimethylformamide containing tetraethylammonium bromide. Other workers[5-11] have stated that reduction of aliphatic carbon–halogen bonds is a two-electron process producing carbanionic intermediates at relatively negative potentials. Among the latter group of reports is the research of Sease and Reed,[7] who conducted a thorough examination of the electrochemical behavior of 1-bromohexane at mercury in dimethylformamide containing tetraethylammonium bromide. These investigators suggested that electrolysis of the alkyl bromide proceeds via a radical intermediate which, if not consumed chemically, is further reduced to a carbanion; protonation of the carbanion by water (present at low concentration in the solvent) affords hexane, and attack of the resulting hydroxide ion on unreduced 1-bromohexane yields 1-hexene and 1-hexanol.

In the work described below, we show that the reduction of 1-iododecane in dimethylformamide containing 0.1 F tetramethylammonium perchlorate and approximately 0.050 M water is a two-electron process at short electrolysis times and at potentials more negative than the polarographic maximum. On the other hand, the results of large-scale electrolyses indicate that the net process involves only one electron at these potentials. These observations, along with the fact that non-linear plots of log *i* vs. *t* are obtained from controlled-potential electrolyses, point toward the occurrence of a chemical reaction which competes with reduction in consuming the alkyl iodide when the electrolysis is carried out slowly. By performing electrolyses of 1-iododecane in the presence of appropriate trapping agents, we have confirmed that decyl carbanions are indeed formed at potentials negative of the polarographic

Table I. Water Content of Dimethylformamide after Various Drying Treatments

treatment	[H$_2$O], mM[a]
(1) no pretreatment of Fisher Spectranalyzed dimethylformamide from freshly opened bottle	39–40
(2) treatment of (1) with Woelm neutral alumina of activity grade I from freshly opened container	47
(3) distillation of (1) from BaO	28
(4) storage of (1) over CaH$_2$	8
(5) storage of (1) over Linde 4A molecular sieves for 5 days	3.5
(6) addition to (5) of supporting electrolyte (0.1 F tetramethylammonium perchlorate)[b]	10
(7) passage of (6) through 8 × 1 in. column of *reactivated* alumina (activity grade I)	5.5
(8) addition of 5 g of *reactivated* alumina (activity grade I) to 35 mL of solution (7) in an air-tight electrolysis cell	1.5–2.0

[a] A concentration of 1 mM is equivalent to approximately 19 ppm H$_2$O. [b] Obtained from the G. Frederick Smith Chemical Co.; used without further purification except for storage in a desiccator.

maximum; in addition, some decyl radicals have been intercepted. Moreover, by doing experiments in a supporting electrolyte–solvent system containing different concentrations of water, we have established that the chemical process which consumes the alkyl iodide during a slow electrolysis and which can make the n value for reduction of 1-iododecane appear to be unity is the interaction between unreduced starting material and hydroxide ion, the latter being generated when decyl carbanions react with water. From the results of chemical and electrochemical measurements we have undertaken, a mechanism can be proposed which satisfactorily accounts for the behavior of 1-iododecane at mercury cathodes as a function of potential, electrolysis time, and concentration of water in the supporting electrolyte–solvent.

Experimental Section

Reagents. Tetramethylammonium perchlorate, purchased from the G. Frederick Smith Chemical Co., was used without additional purification as supporting electrolyte. Commercially available 1-iododecane (Chemical Samples Co., 95%) was purified by means of vacuum distillation.[3] Alumina (ICN Pharmaceuticals, Woelm neutral, activity grade I) was heated at 400 °C in vacuo for 4 h, then cooled, and stored under dry argon. Pure argon used for deaeration was dried by passage through a column of 8-mesh Drierite.

Dimethylformamide (Fisher Spectranalyzed material) was not suitable for use as supplied. Four successive distillations of the solvent at a pressure of 2–3 Torr from calcium hydride, from barium oxide, from a mixture of calcium hydride and tetramethylammonium hydroxide, and finally from barium oxide yielded solvent with virtually none of the N-methylformamide impurity;[3] dimethylformamide freshly distilled in this fashion contains approximately 0.015 M water.

For most of the experiments described in this paper, mercury (Ventron, triply distilled) was utilized without further purification; however, for electrolyses in which removal of traces of water was essential, 50 mL of mercury was predried, before transfer into the electrochemical cell, by being stirred under an argon atmosphere in contact with freshly distilled dimethylformamide and 10 g of activated alumina.

Concerning the Use of Neutral Alumina to Remove Water from Dimethylformamide for Electrochemical Experiments. A number of recent publications[7,12–19] have addressed the problem of preparation of pure, dry dimethylformamide. Among the materials utilized to remove traces of water from dimethylformamide are calcium hydride,[12–15] barium oxide,[12–15] calcium oxide,[12–15] molecular sieves,[7,13,15] and neutral alumina.[15–19] Of particular interest to us is the last reagent, because several workers have reported[17–19] that alumina can be used to obtain very dry solutions for electrochemical experiments.

By using neutral alumina to eliminate almost all traces of water and electrophiles from dimethylformamide containing tetraalkylammonium salts, Parker and co-workers[17,18] were able to record cyclic voltammograms showing reversible redox behavior for several aromatic compounds (anthracene, benzophenone, and nitrobenzene), whereas these electron-transfer processes were previously characterized as irreversible. Removal of water is accomplished by passage of dimethylformamide through a column of neutral alumina[18,19] into the electrochemical cell; to preserve the state of dryness so obtained, more alumina is added to the cell itself. Much of the drying action seems to be lost if the alumina in the cell is not kept in suspension.

Although neither Parker and his collaborators[17,18] nor Moe[19] prescribed any pretreatment of the alumina employed, it was indicated that the alumina should be of activity grade I.[19,20] However, we consider it essential to add that it is virtually mandatory to reactivate such alumina before use. When Woelm neutral alumina (activity grade I) or Fisher neutral alumina (activity grade I) from a previously unopened container is utilized to eliminate traces of moisture from dimethylformamide, either material exhibits little, if any, propensity for water removal.[21] Apparently, such a highly effective desiccant as alumina of activity grade I chemisorbs some water during shipment and storage. We have found that heating the material in vacuo for a period of 4–6 h at 400 °C removes the adsorbed water and ensures the activity of the alumina. This procedure is in accord with methods described in the literature[16,22,23] for preparation of neutral alumina of activity grade I.

Summarized in Table I are results of the determination of water in dimethylformamide subjected to various drying procedures. Measurements of the concentration of water were accomplished with the aid of a Hewlett-Packard 5700A gas chromatograph equipped with a thermal conductivity detector and coupled to a Hewlett-Packard 3380S integrator; samples of the dimethylformamide to be analyzed were injected onto a 6 ft × ⅛ in. column packed with Porapak Q and kept at a temperature of 80 °C. It is evident that alumina pretreated as outlined above and utilized as described by previous investigators[17–19] is a powerful desiccant. Although careful distillation[24] can provide more rigorously dry solvent than that prepared in the present work, the use of alumina is by far the easiest method to obtain dimethylformamide containing less than 2.6 mM (50 ppm) water.

Instrumentation and Procedures. Descriptions of the cells employed for controlled-potential electrolyses[25] and polarographic experiments[26] have been published previously. For cyclic voltammetry, the cell was identical with the polarographic one, except that the dropping mercury electrode was replaced by a Metrohm Model E410 (Brinkmann Instruments, Inc.) hanging mercury drop electrode. 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;[27,28] this electrode has a potential of −0.750 V vs. the aqueous saturated calomel electrode.

Controlled-potential electrolyses were performed with a Princeton Applied Research (PAR) Model 173 potentiostat-galvanostat equipped with a Model 176 current-to-voltage converter to permit monitoring of the cell current on a strip-chart recorder; gravimetric measurement of the area under the current–time curve allowed the coulometric n value to be determined with a precision of ±5%. Use of the iR-compensation capability of the current-to-voltage converter rendered the uncompensated ohmic potential drop negligible. Polarograms were obtained with the aid of a PAR Model 175 universal programmer coupled to the potentiostat-galvanostat. A Sargent-Welch 6-12-s capillary was utilized at a mercury column height of 65 cm; at a potential of −1.1 V in dimethylformamide containing 0.1 F tetramethylammonium perchlorate, the drop time was 4.1 s and $m^{2/3}t^{1/6}$ was 1.15 mg$^{2/3}$ s$^{-1/2}$. Pulse polarograms, in addition to polarograms recorded at controlled drop times, were obtained by use of a PAR Model 174A polarographic analyzer and a PAR Model 174A/70 mechanical drop timer. Triangular waveforms required for cyclic voltammetric experiments were supplied by the PAR Model 175 universal programmer. All polarograms and cyclic voltammograms were recorded on an X–Y recorder.

For the majority of experiments, solutions to be electrolyzed were prepared by dissolution of tetramethylammonium perchlorate in freshly distilled dimethylformamide and were transferred to the assembled electrochemical cell already containing the mercury pool cathode. Then a preelectrolysis was performed at a potential 100 mV

more positive than that needed to reduce the supporting electrolyte, the requisite amount of 1-iododecane was syringed into the cell, and the water content of the solution was checked by means of gas chromatography before the start of the actual electrolysis of the alkyl iodide; the concentration of water was found to be close to 0.050 M.

Conducting experiments under very dry conditions required some special precautions. Freshly distilled dimethylformamide was redistilled from anhydrous copper sulfate (to remove dimethylamine) onto Linde 4A molecular sieves and was stored under argon until use. A 50-mL volumetric flask, fitted with a serum cap, was charged with the appropriate amount of supporting electrolyte in an argon atmosphere. Solvent over molecular sieves was transferred through a cannula to the volumetric flask and the salt was allowed to dissolve. Immediately after being removed from an oven at 150 °C, the cell was assembled and allowed to cool under argon. Next, the supporting electrolyte-solvent was passed through a 8 × 1 in. column of activated alumina directly into the cell, and 10 mL of predried mercury was added to the cell by means of a cannula. Five grams of alumina was added to the cell to maintain the dryness of the solution. After preelectrolysis at a potential 100 mV more positive than the value required to reduce supporting electrolyte, 1-iododecane was syringed into the cell and, before the electrolysis was begun, the concentration of water was determined to be approximately 0.002 M.

During an electrolysis, argon was not bubbled through the solution, but an argon atmosphere was maintained over the solution. Electrolysis was terminated after the current decayed to less than 5% of its initial value, and a known amount of an electroinactive internal standard (phenylcyclohexane) was added to the solution. Then the entire contents of the cell was added to a separatory funnel containing water and diethyl ether, and the products and internal standard were extracted into the ether layer; the alumina and mercury were discarded. Care was taken to ensure that no product escaped as vapor from the separatory funnel; extraction of a standard mixture of products verified that greater than 95% of the products are recovered by this procedure. Finally, the ether extract was analyzed by means of gas chromatography with a Hewlett-Packard 5700A dual-column instrument equipped with a thermal conductivity detector; columns used included a 12 ft × $\frac{1}{8}$ in. stainless-steel column packed with 3% OV-101 on 80-100 mesh Supelcoport and a 12 ft × $\frac{1}{8}$ in. stainless-steel column packed with 3% OV-25 on 100-120 mesh Supelcoport. Peak areas were determined with the aid of a Hewlett-Packard 3380S integrator. In addition, the chromatograph was modified for preparative-scale work in a manner reported elsewhere.[29]

A Varian 220-MHz spectrometer was employed to record NMR spectra, and all chemical shifts are reported in parts per million downfield from tetramethylsilane. Mass spectrometric data were obtained with a Varian CH-7 spectrometer. Gas chromatography-mass spectrometry was performed with a Hewlett-Packard 5710A gas chromatograph coupled to a Hewlett-Packard 5980A mass spectrometer; a 40 m × 0.25 mm i.d. glass capillary column coated with UCON 50-HB-2000 was used in these analyses.

Preparation of $C_8H_{17}CD_2CH_2Br$. Decanal (Aldrich, 10.9 g, 70 mmol) and D_2O (100 g, 5 mol) were dissolved in pyridine that was previously dried over potassium hydroxide, and the solution was stirred at room temperature for 10 days. Then the solution was partitioned between diethyl ether and water; the organic phase was washed repeatedly and was finally dried over magnesium sulfate. A distillation resulted in the recovery of 7.3 g (66%) of decanal: proton NMR ($CDCl_3$) δ 9.73 (s, 1, CHO), 1.57 (t, 2, β-CH₂), 1.25 (broad s, 12, CH₂), and 0.81 (t, 3, CH₃). Only a small resonance for α protons was observed, and integration revealed that the compound was deuterated in the α position to the extent of 93%. This dideuterated aldehyde (6.9 g, 44 mmol) was reduced with lithium aluminum hydride to give 2,2-dideuteriodecan-1-ol in 88% isolated yield. Finally, 6.1 g (38 mmol) of the alcohol was treated with 5.12 g (19 mmol) of phosphorus tribromide to yield 2.5 g (11 mmol, 30%) of 1-bromo-2,2-dideuteriodecane: proton NMR ($CDCl_3$) δ 3.33 (broad s, 2, α-CH₂), 1.20 (broad s, 14, CH₂), and 0.80 (t, 3, CH₃). Mass spectra at 70 eV yielded the following results, relative abundances being reported in parentheses: m/e 224, M⁺ (1.3%); 222, M⁺ (1.0%); 143, M⁺ − Br (1.2%); and 43, $C_3H_7^+$ (100%).

Preparation of $C_9H_{19}CH_2D$. Reaction of 1-bromodecane with magnesium turnings yielded decyl magnesium bromide, which was then quenched by dropwise addition of D_2O. Proton NMR and mass spectrometry revealed that the resulting product was greater than 95% monodeuterated decane.
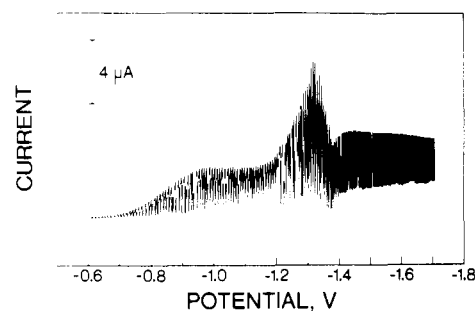

Figure 1. Polarogram for a 0.0010 M solution of 1-iododecane in dimethylformamide containing 0.1 F tetramethylammonium perchlorate and 0.050 M water.

Preparation of $CH_3CD(OH)CH_3$. Spectral-grade acetone was treated with lithium aluminum deuteride in diethyl ether. After the reaction mixture was quenched with water, subsequent distillation yielded the alcohol in 95% amount. No methine resonance was seen in the proton NMR spectrum, and mass spectrometry revealed the expected molecular ion.

Preparation of $CD_2(COOC_2H_5)_2$. Diethyl malonate was treated with pyridine and deuterium oxide, and the mixture was stirred for approximately 3 h. Pentane and diethyl ether were added to extract the dideuterated diethyl malonate, and the organic phase was then dried over magnesium sulfate. Fractional distillation yielded the desired product in greater than 96% purity, as verified by means of proton NMR spectroscopy.

Product Identification. Decane, 1-decene, 1-iododecane, and 1-decanol were identified by comparison of gas chromatographic retention times of electrolysis products with those of commercially available authentic samples. Didecylmercury and N-decyl-N-methylformamide were identified by comparison of their gas chromatographic retention times with verified samples from previous work.[3] Because didecylmercury decomposes to some extent during gas chromatographic analysis, yields of this compound were determined in a special way. Treatment of an ether extract containing all the electrolysis products with a saturated solution of iodine in glacial acetic acid[25,30] resulted in quantitative conversion of didecylmercury to 1-iododecane, and this alkyl iodide can be determined as described above. It is necessary to correct the apparent yield of 1-iododecane, formed from destruction of the organomercury compound, for any unreacted alkyl iodide remaining at the end of the electrolysis by analysis of an aliquot of the untreated product mixture.

Another product, diethyl n-decylmalonate, was identified by comparison of its gas chromatographic retention time and mass spectrum with those of an authentic sample prepared by addition of 1-iododecane to a mixture of sodium ethoxide and diethyl malonate. The desired product was obtained pure by means of distillation: bp 132 °C (1.0 mm); NMR ($CDCl_3$) δ 4.20 (q, 4, COOCH₂), 3.33 (t, 1, CH), 1.93 (m, 2, CH_2CH), 1.29 (m, 22), and 0.88 (t, 3, CH₃). A mass spectrum for the compound obtained at 70 eV provided the following data: m/e 300, M⁺ (0.3%); 255, M⁺ − CH_3CH_2O (9.1%); 227, M⁺ − $COOC_2H_5$ (0.6%); 173, M⁺ − C_9H_{19} (49.2%); and 159, M⁺ − $C_{10}H_{21}$ (100%).

For electrolyses conducted in the presence of deuterium-labeled trapping agents, the quantity of deuterium incorporated into the decane was determined by means of gas chromatography-mass spectrometry. We established the percentage of deuterium incorporation by comparing the ratio of the intensities of the peaks with m/e 142 and 143 for the unknowns to a calibration curve obtained from standards containing various ratios of monodeuterated to undeuterated decane. Results obtained in this fashion had an uncertainty of ±5%.

Results and Discussion

Polarographic and Cyclic Voltammetric Behavior of 1-Iododecane. Figure 1 depicts a polarogram for a 0.0010 M solution of 1-iododecane in dimethylformamide containing 0.1 F tetramethylammonium perchlorate and 0.050 M water. Reduction of the carbon-iodine bond yields a wave with a half-wave potential of −0.86 V. On the plateau of this first wave is a large current maximum,[31] followed by a sharp decline
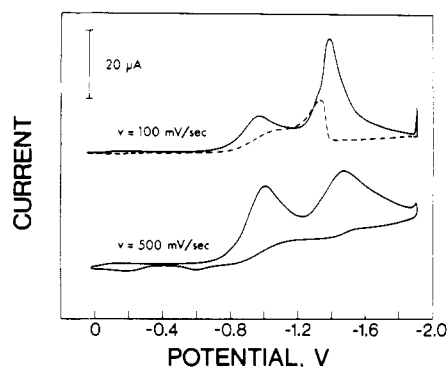
Figure 2. Cyclic voltammograms for a 0.0025 M solution of 1-iododecane in dimethylformamide containing 0.1 F tetramethylammonium perchlorate and 0.050 M water at scan rates of 100 and 500 mV/s; the electrode was a hanging mercury drop with an area of 0.025 cm².
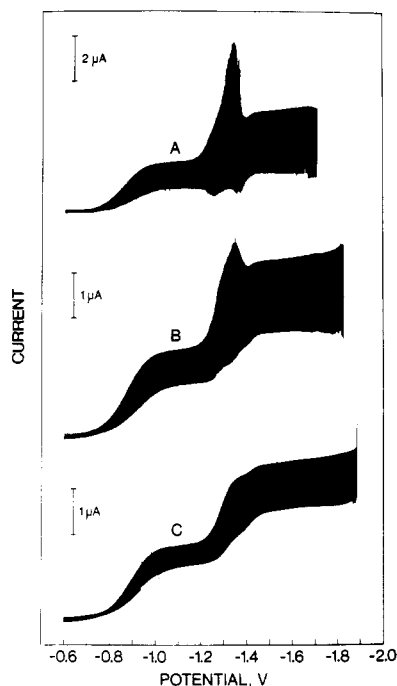

Figure 4. Pulse polarogram for a 0.0010 M solution of 1-iododecane in dimethylformamide containing 0.1 F tetramethylammonium perchlorate and 0.050 M water. A controlled drop time of 2 s was used; the pulse width and sampling period were 56.7 and 16.7 ms, respectively.

Figure 3. Polarograms for a 0.0010 M solution of 1-iododecane in dimethylformamide containing 0.1 F tetramethylammonium perchlorate and 0.050 M water at controlled drop times (curve A, $\tau = 2$ s; curve B, $\tau = 1$ s; curve C, $\tau = 0.5$ s).

and then an increase in current to a new plateau. This behavior can be contrasted to the polarogram presented in our earlier paper dealing with 1-iododecane,[3] for which the limiting current was the same before and after the maximum; differences in the characteristics of the two polarographic capillaries used are responsible for this discrepancy.

As described in our preliminary communication,[1] chronocoulometry and cyclic voltammetry have demonstrated that the duration of electrolysis of 1-iododecane can have a profound effect on the results obtained. Most importantly, a one-electron process takes place at potentials positive of the polarographic maximum regardless of the time scale of the experiment, whereas a two-electron transfer can be observed at potentials negative of the polarographic maximum if the electrolysis time is sufficiently short. For example, at a scan rate of 100 mV/s in dimethylformamide containing 0.1 F tetramethylammonium perchlorate and 0.050 M water, a cyclic voltammogram (Figure 2) for 0.0025 M 1-iododecane shows a wave for reduction of the carbon–iodine bond with a peak potential of −0.96 V, followed by a current spike having
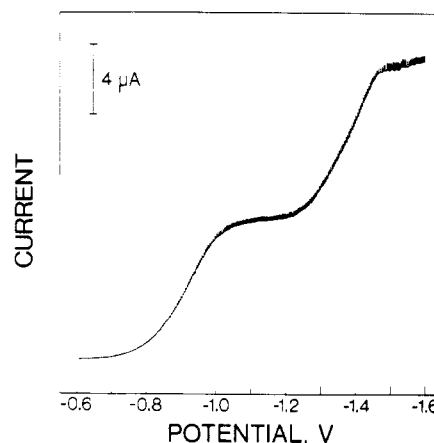
a peak potential of −1.37 V. Upon reversal of the scan, an inverted wave[30,32,33] with a peak potential of −1.33 V appears. Figure 2 also presents a cyclic voltammogram for the same solution with the scan rate increased to 500 mV/s. A pair of irreversible one-electron waves with peak potentials of −0.99 and −1.45 V is seen, but the current spike and inverted wave are absent.

Another illustration of the effect of electrolysis time on the reduction of 1-iododecane emerged from a set of polarograms we recorded by using controlled mercury drop times. Figure 3 shows that, as the drop time is decreased from 2 to 1 s, the polarographic maximum becomes less prominent and the relative height of the second polarographic wave increases. At a drop time of 0.5 s (Figure 3C), two waves of approximately equal height with half-wave potentials of −0.88 and −1.31 V are observed and only a small maximum remains. Furthermore, when a pulse polarogram is recorded (Figure 4) with a pulse width of approximately 56 ms with a 2-s drop time, the polarographic maximum is gone and two waves with half-wave potentials of −0.93 and −1.36 V, each corresponding to a one-electron process, are seen.

Interestingly, the appearance of a pair of one-electron waves in the polarogram for a simple alkyl halide is not in accord with the classic mechanism of von Stackelberg and Stracke,[34] who proposed that the primary radical, being more easily reducible than the starting material, will be immediately converted to the carbanion. Ostensibly, the decyl radical arising from reduction of 1-iododecane in the present study is stabilized sufficiently to allow the two waves to be resolved. This extra stability is probably a result of strong interaction of the decyl radical with the mercury electrode, evidence for this being the isolation of didecylmercury from large-scale electrolyses.[3] A similar argument was given by Fleischmann et al.[35] who suggested that both the product distribution and the number of electrons transferred to alkyl iodides depend on the extent to which radical intermediates are stabilized by interaction with the electrode material. It seems remarkable that no other report of two separate waves for reduction of a primary alkyl iodide has been published.[36] However, we have established that successful observation of two well-resolved waves depends on the experimental conditions employed. Both the identity and concentration of the tetraalkylammonium salt used as supporting electrolyte affect the results, with low concentrations of tetramethylammonium perchlorate providing the best resolution of the two waves. In addition, the dependence of the mechanism on the time scale of the experiment dictates that short electrolysis times be utilized.

Table II. Coulometric Data and Product Distributions for Electrolytic Reduction of 1-Iododecane in Dimethylformamide Containing 0.1 F Tetramethylammonium Perchlorate and Different Concentrations of Water

| run no. | potential, V | *n* value | product distribution, % | | | | |
			decane	1-decene	1-decanol	didecyl-mercury	other
(a) 0.001 M 1-iododecane and 0.050 M water							
1	−1.1	0.88	1		1	99	
2	−1.7	1.08	52	24	2	2	
(b) 0.0025 M 1-iododecane and 0.002 M water							
3	−1.1	0.85	2			93	
4	−1.7	1.49	71	4		3	telomers[a]

[a] A small amount of telomeric species was detected; see reference 3.

Dependence of the *n* Value for Reduction of 1-Iododecane on Electrolysis Time at Potentials Negative of the Polarographic Maximum. Whereas the *n* value for reduction of 1-iododecane at potentials positive with respect to the polarographic maximum is independent of electrolysis time, results obtained by means of chronocoulometry, polarography, cyclic voltammetry, and controlled-potential coulometry reveal that the relative time scale of the techniques is of great significance at potentials negative of the polarographic maximum. For controlled-potential electrolyses performed in supporting electrolyte–solvent containing 0.050 M water with rapid stirring of the solution so that the electrolysis time is no more than 10 min, the *n* value is essentially unity throughout the entire potential region explored.[3] However, the other three methods can be done with much shorter electrolysis times and an *n* value of two can be obtained at potentials negative of the polarographic maximum. These results, in addition to those presented later in this report, suggest that, in experiments of comparatively long duration, 1-iododecane is consumed via a chemical pathway which competes with electrolytic cleavage of the carbon–halogen bond. A coulometric *n* value of approximately one indicates that a substantial fraction of the 1-iododecane reacts chemically whereas the remaining material is reduced in such a fashion that net one-electron reduction of 1-iododecane is observed.

Previous workers[7,37] have suggested that destruction of starting material by an intermediate carbanion is the reason why coulometric *n* values of less than two are obtained. Two experiments have been performed in order to test this proposal. First, for an electrolysis of 0.0025 M $C_8H_{17}CD_2CH_2Br$ at −1.7 V in dimethylformamide containing 0.1 F tetramethylammonium perchlorate and only 0.002 M water, a coulometric *n* value approaching two was found, 2,2-dideuteriodecane was obtained in 89% yield, only very small amounts (<1%) of 1,2,2-trideuteriodecane and 2,2-dideuterio-1-decene were formed, and none of the possible dimer (eicosane) was seen; the decane species were isolated by means of preparative-scale gas chromatography and were subsequently analyzed by means of proton NMR spectroscopy as well as gas chromatography–mass spectrometry. Second, for the reduction at −1.7 V of a relatively high concentration of 1-iododecane (0.040 M) in dimethylformamide containing 0.1 F tetramethylammonium perchlorate and 0.002 M water (conditions which ought to promote even more strongly the interaction of carbanions with unreduced starting material), only small yields of 1-decene (2%) and eicosane (<1%) were found. Thus, the reaction of a decyl carbanion with unreduced decyl halide appears to be of little importance. We propose instead that hydroxide ion, produced by deprotonation of water present in the supporting electrolyte–solvent,[7] reacts with unreduced alkyl halide to form 1-decene and 1-decanol. If decyl carbanions are indeed present, an obvious reagent for their consumption is water remaining in the dimethylformamide. Whereas in an earlier report[3] the source of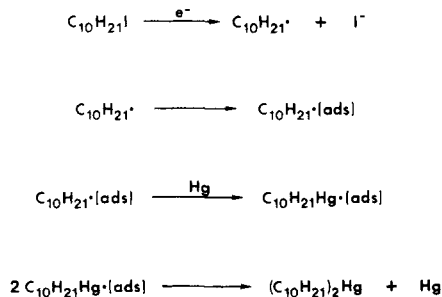 hydroxide ion was believed to be the electrolytic reduction of water, the results described herein indicate that hydroxide results from protonation of anionic intermediates by water.

We have examined the chemical reaction of hydroxide ion with 1-iododecane by using tetramethylammonium hydroxide as the source of the base. In dimethylformamide containing 0.1 F tetramethylammonium perchlorate, 0.005 F tetramethylammonium hydroxide, 0.001 M 1-iododecane, and 0.050 M water, mainly 1-decene is produced, along with a small amount of 1-decanol. This is contrary to results expected for a simple S_N2 reaction and suggests that tetramethylammonium hydroxide may not be highly dissociated in dimethylformamide solutions; this would decrease the nucleophilicity of the base and would enhance the probability of E2 elimination reactions. When 0.001 M 1-iododecane is electrolytically reduced at −1.7 V in dimethylformamide containing 0.1 F tetramethylammonium perchlorate and 0.050 M water, the yield of 1-decene is substantially higher than the amount of 1-decanol (Table II); this observation indicates that hydroxide ion, formed as decyl carbanions are protonated by water, reacts with unreduced alkyl iodide in the same fashion seen in the preceding chemical experiment.

We have done a different chemical experiment by adding *N*-methylformamide to a reaction mixture consisting of 1-iododecane, tetramethylammonium perchlorate, and tetramethylammonium hydroxide; the major product was found to be *N*-decyl-*N*-methylformamide, although small amounts of 1-decene and 1-decanol were obtained. This experiment provides an explanation as to why *N*-decyl-*N*-methylformamide was seen as a side product in our earlier investigation[3] of the electrolysis of both 1-iododecane and 1-bromodecane. Apparently, the *N*-methylformamide (an impurity in some commercially available lots of dimethylformamide) acts as a proton donor for hydroxide ions, and the resulting anion of *N*-methylformamide attacks unreduced decyl halide.

To explore what effects water present in the dimethylformamide has upon the electrolytic reduction of alkyl halides, experiments have been performed with varying amounts of water in the supporting electrolyte–solvent system. In addition, donors of deuterium atoms and deuterium ions have been used to elucidate the mechanism of the reduction in more detail.

Effect of Water on Electrolytic Reduction of 1-Iododecane in Dimethylformamide. Table II summarizes coulometric results and product distributions for controlled-potential electrolyses of 1-iododecane at mercury pool cathodes in dimethylformamide containing 0.1 F tetramethylammonium perchlorate as well as either 0.002 or 0.050 M water. Data for runs 1 and 2 are essentially the same as those obtained in our earlier work.[3] From a comparison of runs 1 and 3, it is apparent that a large decrease in the concentration of water has little effect on results obtained at a potential (−1.1 V) positive of the polarographic maximum; didecylmercury is the only significant product and the *n* value is near unity. However, an examination of the data for runs 2 and 4, which were done at a potential

Scheme I. First Wave (Potentials Positive of Polarographic Maximum)

$$C_{10}H_{21}I \xrightarrow{e^-} C_{10}H_{21}\cdot \ + \ I^-$$

$$C_{10}H_{21}\cdot \longrightarrow C_{10}H_{21}\cdot(ads)$$

$$C_{10}H_{21}\cdot(ads) \xrightarrow{Hg} C_{10}H_{21}Hg\cdot(ads)$$

$$2 \ C_{10}H_{21}Hg\cdot(ads) \longrightarrow (C_{10}H_{21})_2Hg \ + \ Hg$$

(−1.7 V) negative of the polarographic maximum, reveals that there is a substantial change in both the n value and the product distribution. Evidently, when only a small amount of water is present in the supporting electrolyte–solvent, there is little opportunity for abstraction of protons to yield hydroxide ion; consequently, there is less chance for reaction of hydroxide with unreduced 1-iododecane to form 1-decene and 1-decanol, and the increase in the coulometric n value reflects the additional amount of starting material available for electrolytic reduction as opposed to chemical cleavage of the carbon–iodine bond.

Surprisingly, as discussed in the next section, when the concentration of water (in the form of D_2O) is increased to 1 M, the coulometric n value and product distribution mirror closely those seen when only 0.002 M water is present. Differences in the n values and product distributions for 0.050 and 1 M water can be rationalized if one proposes that the hydroxide ion produced by deprotonation of water is well solvated by the water when the latter is present at a concentration of 1 M and, consequently, that the solvated hydroxide ion acts as a noticeably weaker base in causing E2 elimination;[7] thus, more of the 1-iododecane is reduced directly at the electrode. Therefore, the coulometric n value shows a strong dependence on the water content of the supporting electrolyte–solvent, n values greater than one occurring with very low and very high levels of water, and n values near one occurring at intermediate water concentrations.

Controlled-Potential Electrolyses of 1-Iododecane in the Presence of Trapping Agents. Previously reported evidence[7,8,38] for production of carbanionic intermediates during electrolytic reduction of alkyl monohalides has not been conclusive. It was hoped that addition of an excess of diethyl carbonate to the system might allow decyl carbanions to be trapped by attack at the carbonyl site with resultant elimination of ethoxide to give ethyl undecanoate. Accordingly, a 0.0025 M solution of 1-iododecane in dimethylformamide containing 0.1 F tetramethylammonium perchlorate, 0.002 M water, and 0.25 M diethyl carbonate was electrolyzed at −1.7 V. Except for the fact that ethyl undecanoate was found in less than 1% yield, the coulometric n value and product distribution were virtually identical with those obtained under the same conditions (Table II, run 4) in the absence of diethyl carbonate.

Another attempt to detect decyl carbanions involved an experiment performed in the presence of D_2O. A 0.0025 M solution of 1-iododecane in dimethylformamide containing 0.1 F tetramethylammonium perchlorate, 1 M D_2O, and only 0.005 M H_2O was electrolyzed at −1.7 V; the coulometric n value was 1.60 and 82% of the decane was found to be deuterated. Clearly, the use of deuterium oxide as a trap proves that decyl carbanions are intermediates in the electrolytic reduction of 1-iododecane—at least when D_2O is present at a high concentration.

At potentials negative of the polarographic maximum, coulometric n values for the controlled-potential electrolytic

reduction of 1-iododecane are consistently less than two (even in the absence of significant water) and small amounts of didecylmercury and telomers are produced. On the basis of these observations, we suspected that, although most of the 1-iododecane is reduced to carbanions in an overall two-electron step, some decane is formed via one-electron reduction of the alkyl iodide to a radical intermediate which most likely abstracts a hydrogen atom from a molecule of solvent. Electrolysis of a 0.0025 M solution of 1-iododecane in dimethylformamide containing 0.1 F tetramethylammonium perchlorate, 0.25 M $CH_3CD(OH)CH_3$, and 0.25 M H_2O resulted in approximately 11% incorporation of deuterium into the decane formed. Thus, the presence of deuterium in the decane is evidence for the formation of decyl radicals at potentials negative of the polarographic maximum; any decyl carbanions formed should have preferentially abstracted a proton from water or from the hydroxylic moiety of the isopropyl alcohol.
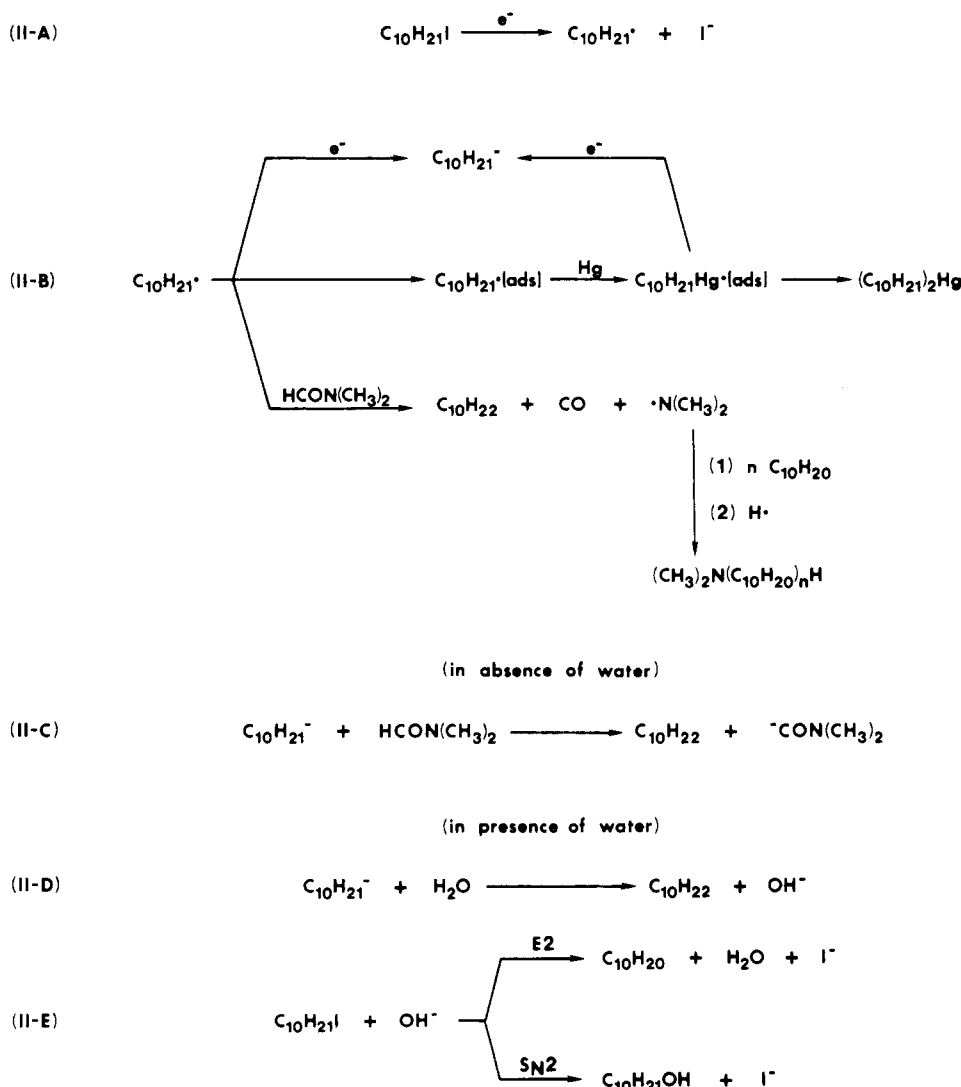
Experiments have been performed in which deuterated diethyl malonate was used instead of deuterium oxide as a possible trap for electrogenerated carbanions. In one experiment, a 0.0025 M solution of 1-iododecane in dimethylformamide containing 0.1 F tetramethylammonium perchlorate, 0.002 M water, and 0.25 M $CD_2(COOC_2H_5)_2$ was electrolyzed at −1.7 V, and the results were as follows: the coulometric n value was 1.53; approximately 17% of the decane had deuterium incorporation, which is consistent with the occurrence of some direct deuteron transfer from $CD_2(COOC_2H_5)_2$ to decyl carbanions; but $C_{10}H_{21}CD(COOC_2H_5)_2$, the adduct arising from attack of $^-CD(COOC_2H_5)_2$ on unreduced 1-iododecane, was found in less than 1% yield. We encountered different results when 0.005 M unlabeled diethyl malonate was present during electrolysis at −1.7 V of a 0.001 M solution of 1-iododecane in dimethylformamide containing 0.1 F tetramethylammonium perchlorate and 0.050 M water; the n value was 1.86 (whereas Table II shows that the n value is only 1.08 if diethyl malonate is absent) and diethyl n-decylmalonate was obtained in 13% yield. In the latter experiment, it appears that hydroxide ion (formed by reaction of electrogenerated decyl carbanions with water) was prevented from attacking unreduced 1-iododecane because diethyl malonate protonated the hydroxide. However, more work is needed before the kinetics and thermodynamics of the various proton-transfer processes taking place in these systems can be fully understood.

Mechanism for the Reduction of 1-Iododecane. Results presented in this paper indicate that the reduction of 1-iododecane at mercury electrodes in dimethylformamide containing 0.1 F tetramethylammonium perchlorate proceeds via a mechanism which is dependent upon potential, electrolysis time, and concentration of water in the supporting electrolyte–solvent system and which involves both decyl radicals and decyl carbanions.

At potentials positive with respect to the polarographic maximum, for which didecylmercury is virtually the only electrolysis product, we proposed earlier[3] that the reduction of 1-iododecane takes place according to Scheme I. Additional work done in the present investigation supports the validity of this mechanistic pathway.

At potentials negative of the polarographic maximum, the production of decyl radical intermediates upon reduction of 1-iododecane has been verified through the use of $CH_3CD(OH)CH_3$ as a deuterium atom donor. Therefore, as shown in Scheme II, the first step in the reduction of the alkyl iodide at these potentials can be formulated as a one-electron transfer to yield a decyl radical (reaction II-A). Once formed, the decyl radicals can participate in several competing processes (reactions II-B): (a) further reduction of the decyl radical, either before or after interaction with mercury, to give the decyl carbanion; (b) adsorption of a decyl radical onto mercury to form didecylmercury, as indicated in Scheme I; and

Scheme II. Second Wave (Potentials Negative of Polarographic Maximum)

(II-A) $\qquad$ $C_{10}H_{21}I \xrightarrow{e^-} C_{10}H_{21}\cdot + I^-$

(II-B) $C_{10}H_{21}\cdot$

$$C_{10}H_{21}\cdot \xrightarrow{e^-} C_{10}H_{21}^- \xleftarrow{e^-}$$

$$C_{10}H_{21}\cdot(ads) \xrightarrow{Hg} C_{10}H_{21}Hg\cdot(ads) \longrightarrow (C_{10}H_{21})_2Hg$$

$$\xrightarrow{HCON(CH_3)_2} C_{10}H_{22} + CO + \cdot N(CH_3)_2$$

$$(1)\ n\ C_{10}H_{20}$$

$$(2)\ H\cdot$$

$$(CH_3)_2N(C_{10}H_{20})_nH$$

(in absence of water)

(II-C) $\qquad$ $C_{10}H_{21}^- + HCON(CH_3)_2 \longrightarrow C_{10}H_{22} + {}^-CON(CH_3)_2$

(in presence of water)

(II-D) $\qquad$ $C_{10}H_{21}^- + H_2O \longrightarrow C_{10}H_{22} + OH^-$

(II-E) $\qquad$ $C_{10}H_{21}I + OH^-$

$$\xrightarrow{E2} C_{10}H_{20} + H_2O + I^-$$

$$\xrightarrow{S_N2} C_{10}H_{21}OH + I^-$$

(c) abstraction of a hydrogen atom from dimethylformamide by a decyl radical to produce decane, after which the solvent-derived radical initiates telomerization of 1-decene.[3,39]

Although it is not possible to state precisely the amount of decyl carbanions formed by reduction of decyl radicals at potentials negative of the polarographic maximum, the results of electrolyses done in the presence of D_2O indicate a lower limit of approximately 80% of the carbanionic intermediate.[40] Protonation of the decyl carbanion by the solvent (reaction II-C) to give decane along with the dimethylcarbamoyl anion[41,42] is highly probable in a system containing a very low concentration of water. In a recent publication by de la Torre and Sease,[43] the role of dimethylformamide as a source of protons for carbanions has been explored. On the other hand, if sufficient water is present, it can protonate the carbanion to yield decane and hydroxide ion (reaction II-D). In turn, reaction of hydroxide with unreduced 1-iododecane produces both 1-decene and 1-decanol (reactions II-E), the E2 elimination being more efficient than the S_N2 process. It is noteworthy that the E2 elimination regenerates water; therefore, when electrolysis of the alkyl iodide is performed slowly, a small amount of water initially present in the supporting electrolyte-solvent can be quite effectual in consuming unreduced 1-iododecane (via reactions II-D and II-E) and in lowering the apparent coulometric *n* value. When electrolysis of 1-iododecane is carried out rapidly at potentials negative of the polarographic maximum (as in the chronocoulometric, cyclic voltammetric, and pulse polarographic experiments

discussed previously) or when the electrolysis is done in virtually dry supporting electrolyte-solvent, the radical intermediates are largely reduced to carbanionic species, chemical consumption of unreduced 1-iododecane by hydroxide ion (from water) does not occur to an appreciable extent, and the coulometric *n* value approaches two.

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Charge Transfer and Partial Oxidation in the Conductive Hydrocarbon–Iodine Complex "2Perylene·3I₂"

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Abstract: It has long been thought that the highly conductive complexes formed between elemental iodine and various polycyclic aromatic hydrocarbons are molecular complexes; i.e., they contain iodine as I₂. In this contribution we report resonance Raman and iodine-129 Mössbauer spectroscopic characterization of the form of the iodine in the most highly conductive of these materials: "2perylene·3I₂". We find that "2perylene·3I₂" is not a molecular complex, but rather a partially oxidized, mixed-valence compound, the charge distribution of which can be approximately formulated on the basis of the spectral data as $(perylene)^{+0.4}(I_3^-·2I_2)_{0.4}$.

Introduction

A question of great current interest in the field of electrically conductive, low-dimensional materials composed of molecular stacks[3] concerns the importance of incomplete charge transfer or "partial oxidation" in facilitating charge transport.[3,4] Considerable experimental and theoretical evidence points to the prerequisite of bringing the arrayed molecules (usually planar, conjugated organics or metal-organics) into formal fractional oxidation states (mixed valency) to help overcome band-filling, bandwidth, and Coulombic impediments to charge conduction along the molecular stack.[3,4] This ionic, mixed valent state is usually brought about via the addition of electron acceptors (or donors) to the system. In apparent contradiction to the above viewpoint stands a large class of highly conductive solids formed by the addition of elemental iodine to various polycyclic aromatic hydrocarbons.[5] In several cases, iodination increases the electrical conductivity of the

hydrocarbon by as much as 10^{12}–10^{14}.[5] These materials have long been formulated as covalently bonded molecular complexes, i.e., unoxidized with iodine present as I₂.

In contrast to the conventional structural model for conductive hydrocarbon–iodine complexes, recent investigations in several laboratories, including our own, have shown that halogenation is an exceedingly effective method for introducing partial oxidation in a number of planar organic and metallo-macrocyclic systems.[6-8] The structures of such materials generally consist of arrays of partially oxidized donor molecules and reduced halogen acceptor counterions.[6-8] In the case of iodine dopants we have also shown that the powerful combination of resonance Raman and iodine-129 Mössbauer spectroscopy can be used to deduce the form of the iodine present in such materials (i.e., I₂, I⁻, I₃⁻, I₅⁻, or mixtures thereof), and thus the degree of partial oxidation.[6a-c,9] This technique is especially informative in instances where disorder[6b] or (as in