compared are either the same or exhibit proportional changes throughout the series. Such an assumption may not be justified.

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Sources of Hydrogen in the Electrochemical Reduction of Iodobenzene in Dimethylformamide Solution

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Abstract: Iodobenzene has been reduced in dimethylformamide solution containing known amounts of H_2O and D_2O; both lithium chloride and tetraethylammonium bromide have been used as electrolytes. The deuterium content of the resulting benzene and the known isotope effect have been used to calculate the fraction of benzene protonated by water. The amount of tetraethylammonium ion losing a proton is given by the yields of triethylamine and ethylene. The results indicate that water is by far the best proton donor present. Tetraethylammonium ion is less effective but can furnish significant quantities of hydrogen ion. However, at least a part of this is done indirectly with water serving as the transfer medium. In the absence of adequate amounts of better proton donors dimethylformamide itself can be a hydrogen source, although benzene yields fall off because of side reactions.

Most work on the electroreduction of the carbon–halogen bond has been concerned primarily with the nature and yield of the products; only recently has there been interest in the source of the hydrogen appearing in the monomeric hydrocarbon that is usually the principal product:

$$R\text{-}\ddot{X}\text{:} + 2e^- + H\text{-}A \rightarrow R\text{-}H + \text{:}\ddot{X}\text{:}^- + \text{:}A^- \qquad (1)$$

Webb, Mann, and Walborsky[1] were among the first to address this problem and used CD_3CN to show that the solvent was the principal hydrogen source in the reduction of 1-bromo-1-methyl-2,2-diphenylcyclopropane in acetonitrile with tetraethylammonium bromide as electrolyte:

$$R\text{-}X \xrightarrow[-X^-]{1e^-} \xrightarrow{1e^-} R\text{:}^- \xrightarrow{CD_3\text{-}CN}{[CD_2\text{-}CN]^-} \rightarrow R\text{-}D \qquad (2)$$
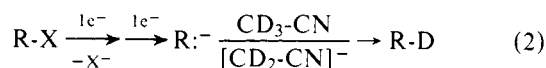
Their results also indicated that, although some of the observed ethylene and triethylamine might have been formed by direct reaction of alkyl carbanion with tetraethylammonium ion

$$R\text{:}^- + [H\text{-}CH_2\text{-}CH_2\text{-}NEt_3]^+ \rightarrow R\text{-}H$$
$$+ CH_2{=\!\!=}CH_2 + NEt_3 \qquad (3)$$
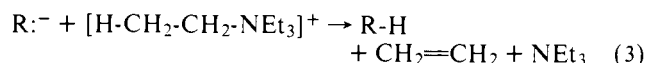
the bulk of these products must have been formed by attack of the solvent anion on tetraethylammonium ion:

$$[CD_2\text{-}CN]^- + [H\text{-}CH_2\text{-}CH_2\text{-}NEt_3]^+$$
$$\rightarrow HCD_2\text{-}CN + CH_2{=\!\!=}CH_2 + NEt_3 \qquad (4)$$
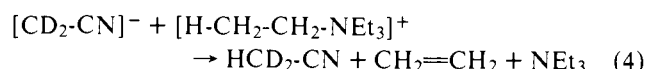
Cockrell and Murray[2] found that reductions of aryl iodides in deuterium oxide–acetonitrile mixtures with lithium perchlorate electrolyte gave efficient deuterium labeling of the resulting aromatic hydrocarbons. The addition of tetraethylammonium perchlorate led to lowered percentages of deuterated product, indicating that tetraethylammonium ion could compete to some extent with deuterium oxide as a hydrogen donor under their experimental conditions. In similar experiments Semmelhack and co-workers[3] prepared labeled spiro compounds by reducing the corresponding chloro compounds in electrolyte

containing deuterium oxide. More recently Grimshaw and Trocha-Grimshaw[4] showed that addition of 1% deuterium oxide to a dimethylformamide–tetrapropylammonium perchlorate system led to deuterium uptake in the reduction of those aromatic halides which would be expected to form carbanion intermediates but not in the cases of those halides which were thought to form radical intermediates.

The dimethylformamide used by electrochemists, although nominally "dry", always contains water. The lowest "guaranteed" water analyses for commercial dimethylformamide are 0.05–0.15% (28–83 mM); the actual water content of freshly opened bottles can be as low as 10 mM and as high as 200 mM.[5] Once a bottle has been opened, the water content can rise rapidly unless effective precautions are taken to prevent moisture uptake during storage and solvent transfer operations.[5,6] With even the very best technique water concentrations of 1–10 mM will prevail during electrolysis. The work reported here was undertaken to study the role of water as a hydrogen source in such water–dimethylformamide mixtures. Although these water concentrations are low, they are comparable to those of the substrates being reduced and water can therefore be expected to play an important part in the chemistry of the system.

In our experiments iodobenzene was electrolyzed in dimethylformamide containing known amounts of H_2O and D_2O.[7] After electrolysis mass spectrometric determination of the deuterium content of the benzene product indicated the extent to which D_2O had been a hydrogen source. The contribution of H_2O was then calculated from the H_2O/D_2O ratio and the relative rates of reaction of the water isotopes. Some experiments were run with lithium chloride electrolyte instead of tetraethylammonium bromide so that water and solvent would be the only possible hydrogen sources. Iodobenzene was selected as substrate, since it reduces sufficiently readily to permit the use of lithium chloride electrolyte instead of tetraethylammonium bromide and since olefin formation by E2 elimination from the substrate is excluded.

Table I. Retention Times (min) in VPC Analyses[a]

	column A	column B
air	1.0	0.75
ethylene	1.0	1.1
water (H_2O or D_2O)	1.8	2.3
benzene (C_6H_6 or C_6H_5D)	1.8	10.5
triethylamine	1.3	19.0
dimethylformamide	5.0	22.0
iodobenzene	8.7_5	100

[a] Column A: 20 ft of 40–60 mesh Fluoropak 80 containing 5% by weight of Carbowax 20M. Column B: 10 ft of 40–60 mesh Fluoropak 80 containing 5% by weight of Carbowax 20M followed by 10 ft of 80–100 mesh Poropak Q. Helium carrier gas at 20 mL/min; injector, columns, and thermal detector at 190 °C; detector bridge current 200 mA.

Experimental Section

Chemicals. Eastman White Label or Aldrich iodobenzene was used as received. Eastman tetraethylammonium bromide was recrystallized from methanolic solution by addition of diethyl ether, dried under vacuum at 120 °C for 10 h, and stored in a drybox.[5] Mallinckrodt Analytical Reagent lithium chloride was dried at 120 °C for 12 h and stored in a drybox. Both Baker Gas Chromatographic and Analyzed Reagent Grade dimethylformamide were used. Solvent which was excessively wet or found to contain polarographically reducible impurities was purified by refluxing for 2 h over Matheson Coleman and Bell 4A molecular sieve (Grade 513, 4–8 mesh) and then distilling under vacuum through a 60 by 1.5 cm helix-packed column. The still-pot temperature was kept below 70 °C at all times to avoid decomposition of the dimethylformamide. Such treatment, if carefully done, reduced the water content to 10 mM or less and in addition removed electroreducible impurities whenever these happened to be present. All storage and transfer of the solvent were carried out in a drybox.

Electrochemical Apparatus and Procedure. The potentiostat was a modification of that described by Underkofler and Shain[8] with a Kronhite DCA-10 amplifier connected as a booster. The cell had a 3.14-cm^2 mercury-pool cathode fitted with a 3 × 10 mm Teflon-coated magnetic stirring bar whose speed was adjusted to approximately 400 rpm. The Cd(Hg)/$CdCl_2$ reference electrode[9] entered the cell through a side arm sealed with a rubber serum cap and an inner silicone washer. Electrical contact with the catholyte was made through a 6-mm diameter by 2-mm Corning "thirsty-glass" tip held in place by a sleeve of shrinkable Teflon tubing. The anode was a coil of silver wire in an anode compartment thich contained the same electrolyte as the cathode compartment; electrical connection was established through four or five 6-mm diameter by 2-mm "thirsty-glass" tips attached to the bottom of the anode sleeve. A side arm at the upper part of the cell led to a small mercury-filled manometer used for measuring the changes in volume due to gas evolution during the electrolysis. Solvent containing electrolyte was stored temporarily over molecular sieve in a 60-mL separatory funnel which drained into the cathode compartment via a small graduated cylinder. Hypodermic needles were used to introduce, or vent, helium through strategically located serum caps for transferring solvent into the graduated cylinder and from there into the cathode compartment, to deoxygenate the catholyte with dry helium, to inject iodobenzene, and to remove analytical samples. At the start of each run the solution was deoxygenated and then electrolyzed at −1.3 V vs. Cd(Hg)/$CdCl_2$ until the current dropped to its residual value of 0.1–0.2 mA. Iodobenzene was then injected and the solution reelectrolyzed until the current had once again dropped to the residual value. The usual sample of 40.8 mg of iodobenzene in 5 mL of electrolyte yielded a substrate concentration of 40 mM.

VPC Analyses. A Gow-Mac 69-500 chromatograph was used with a thermal conductivity detector containing 69-500 rhenium–tungsten WX filaments followed by a Varian Aerograph 600-C flame-ionization detector. Experimental details are summarized in Table 1. Column A was designed for water analysis but its short retention times and good separation of substrate made it very useful for following the progress of electrolyses. Calibration with standard solutions showed that 1–2 mM was the minimum water concentration which could be reliably detected. Column B gave much better product separations

and was used for analyses when electrolysis had been completed.

Isotopic Analyses. Electrolysis solution (5–10 μL) was injected into the liquid inlet of a Hitachi Perkin-Elmer RMU-9L mass spectrometer. The C_6H_6/C_6H_5D ratios were calculated from the relative heights of the m/e 79 and 78 peaks, suitable corrections being made for the P + 1 peak of C_6H_6 at m/e 79 and the P − 1 peak of C_6H_5D at m/e 78. Triethylamine concentration in the electrolysis mixture was determined from the height of its m/e 86 peak, using the sum of the heights of the m/e 78 and 79 peaks for C_6H_6 and C_6H_5D as a reference.

Results and Discussion

Isotope Effect. When both D_2O and H_2O are present, the relative efficiencies of H_2O and D_2O as hydrogen donors must be known if the total contribution of hydrogen by water is to be calculated from the yield of deuterated benzene. This isotope effect is readily obtained from the data of runs 17–20 (Table II), where the total water content was 2 M or greater. Under these conditions no ethylene or triethylamine could be detected and proton donation by tetraethylammonium ion is therefore ruled out. Furthermore, it seems unlikely that dimethylformamide could furnish protons in competition with water when water is present at such high concentrations. This assumption is borne out by the constancy of the calculated C_6H_6/C_6H_5D ratio at $1.2_5 \pm 0.1_6$ throughout the range of 0.5–4.0 M for total water concentration. If dimethylformamide or tetraethylammonium ion were furnishing appreciable quantities of protons, this ratio should increase as the total water concentration and the concentration of D_2O decrease.

Water as a Hydrogen Source. The percentage of benzene obtaining hydrogen from water, calculated as 2.25(% C_6H_5D), shows that at total water concentrations of 0.5 M or greater essentially all of the hydrogen added to the phenyl carbanion came from water (runs 15–20). Only at total water concentrations of 0.2 M or less does the water contribution drop appreciably below 100% (runs 13 and 14). This is accompanied, as would be expected, by an increase in the C_6H_6/C_6H_5D ratio. The appearance of ethylene and triethylamine among the products (runs 11–16) shows that, as the water concentration decreases, the 0.1 M tetraethylammonium ion present in the electrolyte contributes progressively more and more protons to the reduction. The relatively high effectiveness of water as a hydrogen ion donor is evident from its ability to furnish 86–90% of the hydrogen when present at concentrations comparable to those of tetraethylammonium ion (runs 13 and 14).

The results of earlier experiments in which the H_2O concentration was kept to an absolute minimum and varying amounts of D_2O were added are consistent with the results discussed above. Decreasing the D_2O concentration lowers the yield of benzene (runs 1–7) by forcing the phenyl carbanion to go to other, less effective proton donors and thereby facilitating competition by side reactions. This also lowers the percentage of benzene deuterated by D_2O. As would also be expected, the yield of benzene at any given total water concentration is lower with D_2O than with a D_2O–H_2O mixture which contains 50% of the more active isotope. Replacing tetraethylammonium bromide by lithium chloride (runs 8–10) lowers the benzene yield at lower water concentrations by removing tetraethylammonium ion, which, although not as good as water, is still a much better source of protons than is dimethylformamide. One might expect that, in lithium chloride solution, D_2O would compete more effectively with dimethylformamide than with the tetraethylammonium ion of the other electrolyte and the percentage of C_6H_5D should therefore be higher; just the opposite occurs. Possible reasons for this are suggested in the section dealing with the role of dimethylformamide.
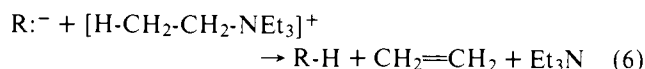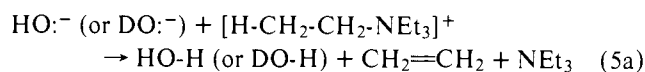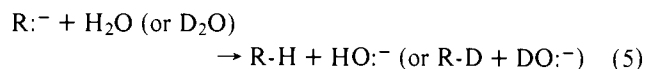
Tetraethylammonium Ion as a Hydrogen Source. The analytical values for ethylene and triethylamine, although not in

Table II. Results of Electrolysis Experiments

run	supporting electrolyte	[H₂O], mM	[D₂O], mM	benzene yield, %ᵃ	C₆H₅D in product, %ᵇ	[C₆H₆]/ [C₆H₅D]	benzene receiving hydrogen from water, %ᵇ,ᶜ	ethylene yield, %ᵇ	triethyl- amine yield, %ᵇ
1–3	0.1 M TEABᵈ	2	0	71–78	0			66–90	49–67
4	0.1 M TEAB	2	100	81	64	0.61	65		
5	0.1 M TEAB	2	200	85	74	0.35	75		
6	0.1 M TEAB	2	500	90	76	0.32	76		
7	0.1 M TEAB	2	1000	87	81	0.23	81		
8	0.5 M LiCl	2	0	58	0				
9	0.5 M LiCl	2	100	70	53	0.89	54		
10	0.5 M LiCl	2	1000	91	74	0.35	74		
11	0.1 M TEAB	7	0	72				82	98
12	0.1 M TEAB	11	0	78				68	
13	0.1 TEAB	23	23	84	38	1.62	86	78	88
14	0.1 M TEAB	105	105	90	41	1.46	90	65	67
15	0.1 M TEAB	260	260	95	44	1.30	98	52	45
16	0.1 M TEAB	535	535	94	45	1.21	102	35	27
17	0.1 M TEAB	1010	1010	96	45	1.22	101	0	0
18	0.1 M TEAB	1760	1760	93	44	1.26	98	0	0
19	0.1 M TEAB	1820	1820	95	46	1.18	103	0	0
20	0.1 M TEAB	1920	1920	85	43	1.34	96	0	0

ᵃ Referred to starting material. ᵇ Referred to benzene product. ᶜ Calculated as 2.25 (% C₆H₅D in product). ᵈ TEAB = tetraethylammonium bromide.

perfect agreement, nevertheless show clearly that tetraethylammonium ion becomes a significant source of protons when the water concentration is 1 M or less (runs 11–16). However, the evidence requires that only part of this hydrogen go to benzene, the remainder being used to convert hydroxide ion back to water. First, there is no appreciable departure from a C_6H_6/C_6H_5D ratio of $1.2_5 \pm 0.1_6$ at total water concentrations of 0.5 and 1.0 M (runs 15 and 16), even though the amounts of tetraethylammonium ion decomposing to ethylene and triethylamine correspond to 25–50% of the benzene formed. Second, throughout the range of 0.05–1.0 M total water concentration (runs 13–16) the sum of the amount of benzene obtaining hydrogen from water plus the amount of tetraethylammonium ion decomposed is far greater than either the amount of benzene formed or the amount of iodobenzene reduced. This is convincing evidence for two competing paths for hydrogen transfer (reactions 5 and 6). Because of reaction 5a tetraethylammonium ion can be the ultimate hydrogen source even though the hydrogen ion is actually transferred to the phenyl carbanion by water:

$$R:^- + H_2O \text{ (or } D_2O)$$
$$\rightarrow R\text{-}H + HO:^- \text{ (or } R\text{-}D + DO:^-) \quad (5)$$

$$HO:^- \text{ (or } DO:^-) + [H\text{-}CH_2\text{-}CH_2\text{-}NEt_3]^+$$
$$\rightarrow HO\text{-}H \text{ (or } DO\text{-}H) + CH_2\!\!=\!\!CH_2 + NEt_3 \quad (5a)$$

$$R:^- + [H\text{-}CH_2\text{-}CH_2\text{-}NEt_3]^+$$
$$\rightarrow R\text{-}H + CH_2\!\!=\!\!CH_2 + Et_3N \quad (6)$$

The 38% value for C_6H_5D in the benzene obtained in run 13 requires that direct transfer of a proton from tetraethylammonium ion occur to the extent of only 14% of the product even at a water concentration of but 0.05 M, just half that of the tetraethylammonium ion. The amounts of ethylene and triethylamine formed are actually far greater than this, so that a considerable amount of these products must be contributed by the reaction of tetraethylammonium ion with hydroxide ion (reaction 5a). This possibility was confirmed by separate experiments which showed that 0.1 M tetraethylammonium ion in dimethylformamide did not react with hydroxide ion when the water concentration was high (2–4 M) but formed ethylene

and triethylamine quite rapidly when the water concentration was low ($\leq$0.1 M). A similar behavior in acetonitrile has been observed by Webb, Mann, and Walborsky,[1] who found that $[CD_2CN]^-$ formed in the initial hydrogen ion transfer reacts subsequently with tetraethylammonium ion to yield ethylene and triethylamine. The approximate ratios of the rates of hydrogen ion transfer by water and by tetraethylammonium ion can be calculated to be 12:1 and 5:1 from the results of runs 13 and 14, respectively. There is incidentally no reason to expect this ratio to be constant with changing water concentration; adsorption and double-layer effects can lead to concentrations at, or near, the electrode surface that are quite different from those in the body of the solution.

Role of Dimethylformamide in the Reduction. When only lithium chloride and small amounts of water are present during the electrolysis, dimethylformamide must furnish hydrogen to the phenyl carbanion or react with it in some other way. An extreme example is run 8, in which 0.12 mmol of benzene was formed in a solution that had contained only 0.01 mfw of H_2O at the beginning of the electrolysis; under these conditions the yield of benzene was but 58%. Runs 9 and 10 with D_2O concentrations of 0.1 and 1.0 M gave yields that were considerably higher but still well below 100% and noticeably lower than those obtained with comparable water concentrations in the presence of tetraethylammonium ion (runs 13, 14, and 16). These results require three separate modes of reaction for the phenyl carbanion in this lithium chloride–dimethylformamide system: (1) extraction of hydrogen ion from water (reaction 5), (2) extraction of a proton from dimethylformamide

$$R:^- + H\text{-}CO\text{-}NMe_2 \rightarrow R\text{-}H + [:CO\text{-}NMe_2]^- \quad (7)$$

and (3) reaction with dimethylformamide to yield other products.

Although direct deuteron transfer by D_2O is responsible for 53 and 74% of the benzene formed in runs 9 and 10, this reaction is competitively much less effective in lithium chloride solution than in solutions which contain tetraethylammonium bromide electrolyte (runs 13, 14, and 16). One factor undoubtedly contributing to this striking decrease in water's ability to furnish hydrogen ion is the strong interaction between water and lithium ions. Another factor, important at low water
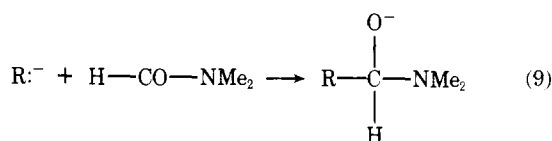
concentrations, is the absence of a reaction for regenerating water which could play a role comparable to that of reaction 5a in fairly dry tetraethylammonium bromide solution. The equilibrium

$$HO^- \text{ (or } DO^-) + H\text{-}CO\text{-}NMe_2 \rightleftharpoons HO\text{-}H \text{ (or } DO\text{-}H)$$
$$+ [:CO\text{-}NMe_2]^- \quad (8)$$
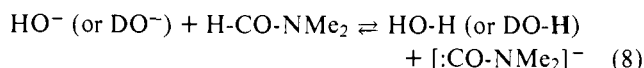
certainly lies far to the left and hydroxide ion, formed when water transfers a hydrogen ion to a phenyl carbanion, cannot be readily converted back to water, as is the case when tetraethylammonium ion is present.

In runs 9 and 10 the nondeuterated benzene must have obtained almost all its protons directly from dimethylformamide (reaction 7), since deuterium would have been introduced by an indirect transfer (reaction 5 followed by reaction 8). The unfavorable equilibrium in reaction 8 also argues against the possibility of an indirect transfer. Further work is needed to establish which protons, "carbonyl" or "amide", are the reactive ones.

Another possible mode of reaction for the phenyl carbanion is addition to the carbonyl group of dimethylformamide (eq 9). We have detected small amounts of dimethylamine and

$$R{:}^- + H\text{—}CO\text{—}NMe_2 \longrightarrow R\text{—}\overset{\displaystyle O^-}{\underset{\displaystyle H}{\overset{\displaystyle |}{\underset{\displaystyle |}{C}}}}\text{—}NMe_2 \quad (9)$$

benzaldehyde in exploratory experiments but as yet have not had the opportunity to look systematically for byproducts which might result from such an addition.

After this work had been completed, Peters et al.[10] reported finding 0.002–0.05 mol % N-methylformamide (0.2–7 mM) in commercial grades of N,N-dimethylformamide. There is no question that the amide hydrogen of methylformamide is much more acidic than the carbonyl hydrogen of either methylformamide or dimethylformamide and would therefore donate protons more rapidly. However, we are currently using the same brands and grades of dimethylformamide as were used in the work reported here and find the monomethylformamide concentration to be consistently below 0.1 mM, our limit of detection.[11] This concentration is so much smaller than the amount of iodobenzene taken for reduction—40 mM in most experiments—that, even if all of the amide hydrogen had been consumed, dimethylformamide would still have to be the primary source of hydrogen.

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Electrochemical Behavior of Tetrathiafulvalene–Tetracyanoquinodimethane Electrodes in Aqueous Media

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Abstract: Compacted pellets of tetrathiafulvalene–tetracyanoquinodimethane (TTF–TCNQ) were prepared and the properties of this material as an electrode in aqueous media were investigated. The electrode was stable over a potential range of about 0.9 V; within this region the electrode exhibited residual faradaic currents of less than 1–2 $\mu A/cm^2$ and the oxidation and reduction of soluble redox couples at this electrode could be carried out. Upon exceeding the potential limits of stability of the electrode, the subsequent voltammograms showed symmetrical peaks attributable to insoluble compounds of TTF or TCNQ and supporting electrolyte ions (e.g., TTFBr, KTCNQ). The redox reaction of these species could also be observed in the cyclic voltammograms.

Introduction

TTF–TCNQ and other organic metal-like compounds[1,2] have been the subject of extensive investigation by many groups.[3-7] For TTF–TCNQ most of the studies have concerned electrical and magnetic properties, crystal binding energies, and degree of charge transfer in the material. While there have been a few electrochemical studies of TTF and TCNQ compounds,[8-12] no studies have been reported concerning the utilization of TTF–TCNQ or other metal-like organic compounds as electrode materials. Only recently have the electrode properties of polymeric sulfur nitride, $(SN)_x$, been described.[13] While the properties and design of these organic metal-like