lends some support to either of our tentative assignment of the 700-nm band. It should be noted that CIDNP studies of iodine atom exchange between carbon-centered radicals would require $CH_3\dot{I}CH_3$ to have a lifetime no longer than a few microseconds.[30a,e] This is not inconsistent with our observations.

Discussion

Charge-transfer absorptions are observed whenever nitroxides are dissolved in polyhalogenated solvents. Laser irradiation at wavelengths within these bands "instantaneously" yields the corresponding oxoammonium halide and a carbon-centered radical via a photoinduced electron transfer followed by loss of halide ion, just as was first proposed by Koch and co-workers[9] for the specific case of di-*tert*-butyl nitroxide in CCl_4. This phenomenon indicates that care must be exercised in the choice of solvent during photochemical studies which directly involve nitroxides (e.g., the quenching of other molecules in photoexcited singlet and triplet states) or which involve them indirectly (e.g., the spin-trapping of photo-generated radicals by nitrones and nitroso compounds).

The "instantaneous" production of oxoammonium halides will make time-resolved kinetic studies on these species relatively simple. Similarly, a straightforward method for the "instantaneous" production of haloalkyl radicals may prove valuable in other kinetic studies.

Experimental Section

TEMPO (Aldrich) was purified by multiple sublimations. Di-*tert*-butyl nitroxide was used as received. All solvents were Aldrich gold-label grade. CCl_4 was distilled from K_2CO_3. The bromides and methyl iodide were passed through alumina (Aldrich, Brockman I, neutral, activated aluminum oxide) prior to use.

The 337- and 308-nm[33] and the 355-nm LFP equipment with nanosecond[34] and picosecond[35] time resolution have been described previously.

Acknowledgment. We thank Dr. J. C. Scaiano for a generous allotment of time on his LFP equipment and the Office of Basic Energy Sciences of the US Department of Energy which supported (in part) the work done at Notre Dame Radiation Laboratory (Document No. NDRL-3211).

Registry No. 1, 26864-01-7; TEMPO, 2564-83-2; CCl_4, 56-23-5; $Cl_3C^\bullet$, 3170-80-7; $Cl_3COO^\bullet$, 69884-58-8; $CHCl_3$, 67-66-3; $CF_2ClCFCl_2$, 76-14-2; CH_2Cl_2, 75-09-2; CH_2Br_2, 74-95-3; $CHBr_3$, 75-25-2; C_2H_5Br, 74-96-4; $C_6H_5CH_2Br$, 100-39-0; CH_3I, 74-88-4; di-*tert*-butyl nitroxide, 2406-25-9; 4-hydroxy-2,2,6,6-tetramethylpiperidine-*N*-oxyl, 2226-96-2; 1,1,3,3-tetramethylisoindolyl-*N*-oxyl, 80037-90-7; 1-oxo-2,2,6,6-tetramethylpiperidinium, 124340-45-0.

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Electrochemical Reduction of 4-Iodo- and 4-Bromoanisole at Mercury and Carbon Cathodes in Dimethylformamide

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In dimethylformamide containing tetramethylammonium perchlorate, cyclic voltammograms for reduction of 4-iodo- and 4-bromoanisole at mercury and carbon electrodes exhibit single irreversible waves corresponding formally to two-electron cleavage of the carbon–halogen bond. In preparative-scale controlled-potential electrolyses of 4-iodoanisole at mercury pool cathodes, a two-to-one mixture of anisole and bis(*p*-anisyl)mercury is obtained at potentials close to the peak potential, whereas anisole is the only species formed at more negative potentials. Reduction of 4-iodoanisole at mercury appears to proceed via *p*-anisyl radicals that (i) yield adsorbed *p*-anisylmercury radicals which disproportionate to give bis(*p*-anisyl)mercury or (ii) undergo further reduction, followed by protonation, to afford anisole. Electrolyses of 4-iodoanisole at carbon electrodes, as well as reduction of 4-bromoanisole at both mercury and carbon, result solely in the production of anisole; presumably, even if *p*-anisyl radicals are generated transiently, they undergo facile reduction to *p*-anisyl carbanions, which are protonated immediately to yield anisole.

There have been numerous publications[1-15] dealing with the electrochemistry of unsubstituted and substituted monohalobenzenes. Whereas most of the papers are concerned either with the effect of various substituents on the polarographic characteristics of monohalobenzenes or with

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the kinetics of both homogeneous and heterogeneous electron-transfer processes attending the reduction of such compounds, only a few reports[12-15] have appeared in which products derived from the direct electrolytic reduction of monohalobenzenes were determined quantitatively.

In a review by Hawley,[16] the polarography of iodobenzene, bromobenzene, and chlorobenzene is discussed, and it is stated that the pathway for reduction of each compound apparently involves (i) two-electron cleavage of the carbon–halogen bond to produce the phenyl carbanion and a halide ion and (ii) rapid protonation of the carbanion to yield benzene. However, Hawley points out that the unusual ease with which iodobenzene is reduced at mercury suggests the possible intermediacy of organomercury species, although no experimental evidence in support of this hypothesis has heretofore been published.

Reed[12] performed controlled-potential electrolyses of iodo-, bromo-, and chlorobenzene at mercury pool cathodes in dimethylformamide containing tetraethylammonium bromide; he observed that each compound undergoes a net two-electron reduction with quantitative formation of benzene. In a study by Cockrell and Murray,[13] *o*-iodotoluene as well as the family of iodoanisoles was reduced at mercury electrodes in acetonitrile containing deuterium oxide in order to produce the corresponding monodeuterated aromatic species in high yield, but no information was provided concerning either the potential employed or the number of electrons involved in cleavage of the carbon–iodine bond. To assess the importance of different sources of protons (water, supporting electrolyte, and solvent) for electrogenerated phenyl carbanions, de la Torre and Sease[14] measured the extent of deuterium incorporation into the benzene derived from two-electron reduction of iodobenzene at mercury in dimethylformamide containing various concentrations of deuterium oxide; in some experiments, particularly those with small amounts of water, the recovery of benzene (nondeuterated and monodeuterated) was significantly less than 100%, but no other products were reported to be present. Finally, in a study of the reduction of chlorobenzene at mercury in dimethyl sulfoxide containing tetraethylammonium bromide, Farwell, Beland, and Geer[15] concluded that benzene is formed quantitatively via a process involving two-electron cleavage of the carbon–chlorine bond.

In addition to the preceding electrochemical investigations, several reports[17-19] pertaining to the chemical reduction of aryl monohalides by reagents such as sodium naphthalenide have revealed the formation of biaryl compounds as products and have raised questions as to whether those species arise via coupling of aryl radicals or via attack of an aryl carbanion on unreduced aryl monohalide. In a related study by Asirvatham and Hawley,[20] evidence was offered that electrochemical reduction of *p*-fluorobenzonitrile at platinum in dimethylformamide containing tetraethylammonium perchlorate leads to the production of 4,4′-dicyanobiphenyl via combination of electrogenerated *p*-fluorobenzonitrile radical-anions.

In the present work, we have utilized cyclic voltammetry and chronoamperometry to examine the electrochemical reduction of 4-iodo- and 4-bromoanisole at mercury and carbon cathodes in dimethylformamide containing tetramethylammonium perchlorate and, through the use of preparative-scale controlled-potential electrolysis, we have identified and quantitated the products that form at different potentials. Our decision to study the behavior of 4-iodo- and 4-bromoanisole stems from the fact that the starting materials as well as their electrolysis products are less volatile and easier to quantitate than the species encountered when iodo- and bromobenzene are investigated. On the basis of our findings, a plausible mechanism can be postulated to account for the formation of the various products. This information is relevant because we are seeking to extend the work of Matsue, Kitahara, and Osa,[21] who explored the reaction of electrogenerated phenyl carbanions with carbon dioxide to yield benzoic acid.

Experimental Section

Reagents. Dimethylformamide used as solvent throughout this work was Burdick and Jackson "distilled in glass" material; it was stored under argon and over 4-Å molecular sieves. Tetramethylammonium perchlorate employed as supporting electrolyte was obtained from the G. Frederick Smith Chemical Co.; prior to being used, it was recrystallized from distilled water and was dried for at least 48 h in a vacuum oven at 70 °C. Commercially available 4-iodo- and 4-bromoanisole were purchased from Aldrich Chemical Co. and were used without additional purification. Deaeration of all solutions for electrochemical experiments was accomplished with Air Products UHP argon.

Instrumentation and Procedures. Previous publications[22,23] contain descriptions of cells and procedures for cyclic voltammetry, chronoamperometry, and controlled-potential coulometry. Working electrodes for cyclic voltammetry and chronoamperometry were prepared from either triple-distilled mercury (Troy Chemical Corp., Wood Ridge Chemical Division) or glassy carbon rod (Tokai Electrode Manufacturing Co., Tokyo, Japan, Grade GC-20), which was press fitted into a shroud of Kel-F. Mercury pool cathodes for controlled-potential electrolyses consisted of the same material as specified above. Reticulated vitreous carbon (RVC 2X1-45S), purchased from The Fluorocarbon Co. (Anaheim, CA), was cut into disk-shaped working electrodes for large-scale electrolyses; procedures for pretreatment of the carbon electrodes are described elsewhere.[24] All potentials in this paper 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;[25,26] this electrode has a potential of −0.75 V versus the aqueous saturated calomel electrode at 25 °C.

Controlled-potential electrolyses were accomplished with the aid of a Princeton Applied Research Corporation (PARC) Model 173 potentiostat–galvanostat equipped with a PARC Model 176 current-to-voltage converter that provided *iR* compensation; current–time curves for the electrolyses were monitored with an Esterline-Angus L1101S strip-chart recorder, and current–time integrals were determined with a house-built digital coulometer.[27] Cyclic voltammograms were obtained by use of a PARC Model 175 Universal Programmer coupled to the potentiostat–galvanostat and were recorded with a Houston Instruments Model 2000-5-5 X–Y plotter. Chronoamperometric experiments were conducted with the aid of locally written software, which controlled a Tecmar data acquisition board installed in an IBM-PC computer; other details about the chronoamperometric measurements are presented elsewhere.[27]

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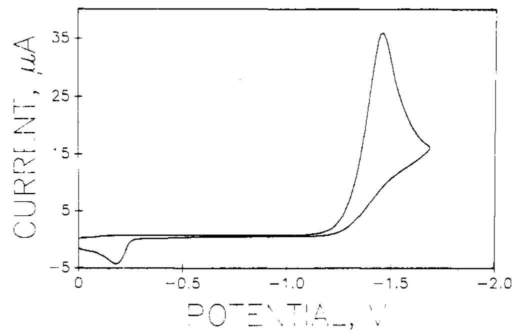

Figure 1. Cyclic voltammogram obtained at a scan rate of 200 mV s^{-1} for reduction of 2.5 mM solution of 4-bromoanisole at a hanging mercury drop electrode (area = 0.014 cm^2) in dimethylformamide containing 0.1 M tetramethylammonium perchlorate.

Gas chromatography for the separation, identification, and quantitation of electrolysis products was accomplished with a Varian Model 3700 dual-column instrument equipped with flame ionization detectors. Gas chromatographic peak areas were measured with the aid of a Hewlett-Packard Model 3380S integrator. Columns used were a 10 m × 0.53 mm, wide-bore capillary column (RSL-300, Alltech Associates) that utilizes polyphenylmethylsiloxane as stationary phase and a 51 cm × 3.1 mm stainless steel column packed with 3% OV-101 on 100–120-mesh Chromosorb WHP. A known quantity of an electroinactive internal standard (dodecane) was added to each sample solution prior to the start of an electrolysis, so that the yield of each product could be determined. All product yields tabulated in this paper represent the absolute percentage of starting material incorporated into a particular species.

Product Identification and Determination. Anisole was identified as an electrolysis product by comparison of its retention time with that of a commercially available authentic sample. In similar fashion, bis(*p*-anisyl)mercury was identified as a product by comparison of its retention time with that of the pure compound synthesized from sodium metal, 4-bromoanisole, and elemental mercury.[28,29] The electrolyzed solution containing the products (and the internal standard) in dimethylformamide was partitioned between diethyl ether and saturated aqueous sodium chloride solution to determine the yield of bis(*p*-anisyl)mercury. Next, a portion of the ether phase was treated with a saturated solution of iodine in glacial acetic acid, which results in the quantitative conversion of bis(*p*-anisyl)mercury to 4-iodoanisole.[30] After the ether phase was dried over anhydrous magnesium sulfate and subjected to gas chromatographic analysis, the area of the peak for 4-iodoanisole (corrected, if necessary, for any starting material not electrolyzed) was correlated with the amount of diorganomercury species formed electrolytically.

Results and Discussion

Cyclic Voltammetric Behavior of 4-Bromoanisole at Mercury. Figure 1 shows a cyclic voltammogram for reduction of a 2.5 mM solution of 4-bromoanisole at a hanging mercury drop electrode in dimethylformamide containing 0.1 M tetramethylammonium perchlorate that was recorded at a scan rate of 200 mV s^{-1}. For concentrations of 4-bromoanisole from 1 to 5 mM, and for scan rates ranging from 20 to 200 mV s^{-1}, $i_p/v^{1/2}C$ was found to be essentially constant. In addition, the peak potential for reduction of 4-bromoanisole, seen to be −1.47 V in Figure 1, shifts negatively by approximately 78 mV for a 10-fold increase in scan rate. These observations are fully consistent with the conclusions of earlier workers that reductive cleavage of the carbon–halogen bond of an aryl halide is a one-step, irreversible, two-electron process.[1-15]

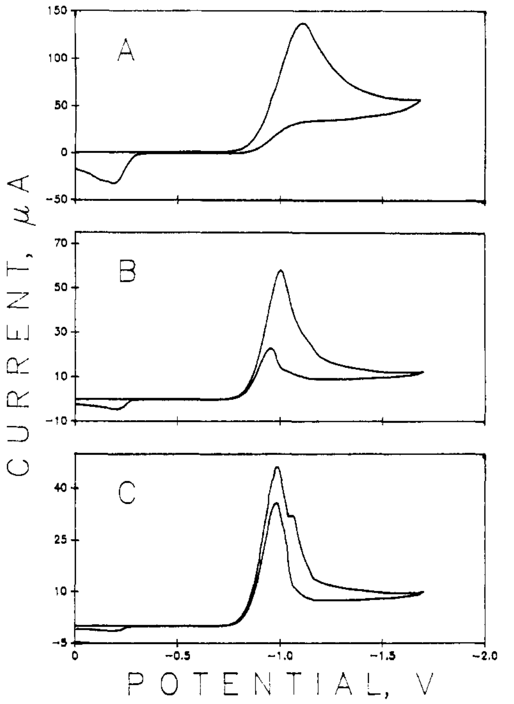

Figure 2. Cyclic voltammograms for reduction of a 5.0 mM solution of 4-iodoanisole at a hanging mercury drop electrode (area = 0.014 cm^2) in dimethylformamide containing 0.1 M tetramethylammonium perchlorate. Curve A: scan rate = 2 V s^{-1}. Curve B: scan rate = 100 mV s^{-1}. Curve C: scan rate = 50 mV s^{-1}.

In Figure 1, a small anodic wave is seen at approximately −0.18 V on the positive-going scan of the cyclic voltammogram for 4-bromoanisole. As discussed in a previous publication,[22] the process responsible for this wave appears to be oxidation of mercury in the presence of trimethylammonium methylide, arising because electrogenerated carbanions deprotonate the tetramethylammonium cation of the electrolyte.[31] Oxidation of mercury in the presence of bromide, released upon reduction of 4-bromoanisole, cannot account for the anodic wave at −0.18 V; bromide-assisted oxidation of mercury in dimethylformamide is known to yield a pair of reversible waves at +0.56 and +0.91 V.[22,32]

Cyclic Voltammetric Behavior of 4-Iodoanisole at Mercury. We have discovered that the cyclic voltammetric characteristics of 4-iodoanisole at a hanging mercury drop are more complicated than the simple picture portrayed above. Although further investigation is planned, we wish to describe here certain features of this behavior that bear most strongly on the principal subjects of this paper, namely, (i) the identification and quantitation of products derived from electrolyses of 4-haloanisoles and (ii) the elucidation of the mechanism for reduction of 4-haloanisoles.

Illustrated in Figure 2A is a cyclic voltammogram recorded at a scan rate of 2 V s^{-1} for reduction of a 5.0 mM solution of 4-iodoanisole at a hanging mercury drop electrode in dimethylformamide containing 0.1 M tetramethylammonium perchlorate; except for the fact that the peak potential is −1.10 V, there is little to distinguish Figure 2A from Figure 1. However, at slower scan rates,

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several unusual features develop. First, at potentials more negative than the peak potential, the current exhibits an abnormal decay (Figures 2B and 2C), suggesting that the electrode surface is at least partially blocked with respect to continued diffusion-controlled reduction of 4-iodoanisole. A similar observation has recently been made for the reduction of 1,10-diiododecane at mercury in dimethylformamide containing tetramethylammonium perchlorate; for the latter system, reduction of the starting material is greatly inhibited by formation of an organomercury polymer.[33] Second, in Figure 2B is seen a small *cathodic* peak, somewhat gaussian in shape, on the *positive-going* scan, and this phenomenon becomes more pronounced at lower scan rates (Figure 2C); such *inverted* waves, reported for reduction of several alkyl halides[30,34] as well as other species[35-39] at mercury, have been associated with adsorption of radicals, with unblocking of an electrode surface by oxidation of a tetraalkylammonium amalgam, and with movements of the mercury surface caused by inhomogeneous polarization and adsorption. Third, notice that Figure 2C, a cyclic voltammogram recorded at a scan rate of 50 mV s^{-1}, exhibits two cathodic waves—a larger peak at −0.97 V and a smaller shoulder at −1.05 V; at a scan rate of 20 mV s^{-1}, the relative heights of these two waves are reversed (and the peak potentials are shifted approximately 50 mV in the positive direction). It is well known that, when reduction of a compound gives rise to a product that can exist in both adsorbed and solution-soluble states and when the strength of adsorption is sufficient, two discrete cyclic voltammetric waves are seen; the first wave, commonly termed a pre-peak, is attributable to formation of the adsorbed product, whereas the second wave is due to the formation of the soluble product.[40] Moreover, when the scan rate is increased for a given concentration of starting material, or when the concentration of starting material is decreased at a fixed scan rate, the height of the pre-peak increases with respect to that of the second wave.[40] It is tempting to conclude from the cyclic voltammogram shown in Figure 2C that reduction of 4-iodoanisole leads to an adsorbed product as well as a soluble product. However, adsorption processes ordinarily manifest themselves in cyclic voltammetric experiments when the concentration of electroactive species is comparatively low (<1 mM), whereas Figure 2C pertains to a 5 mM concentration of 4-iodoanisole—though we have recorded cyclic voltammograms for concentrations of 4-iodoanisole as low as 0.2 mM that resemble Figure 2C qualitatively. In addition, cyclic voltammograms, obtained sequentially with fresh hanging mercury drop electrodes in a given solution of 4-iodoanisole and under otherwise identical conditions, lack reproducibility in that (i) the degree of separation of the two waves is not always the same and (ii) the relative peak currents may be different. Nevertheless, when taken together, the results of the cyclic voltammetric experiments provide strong evidence that the pathway for reduction of 4-iodoanisole at mercury involves an adsorbed intermediate.

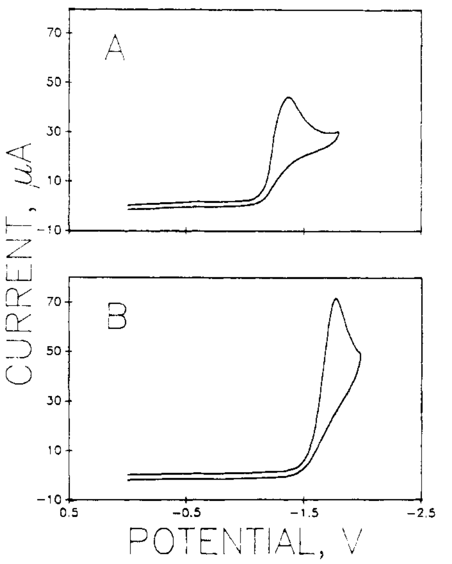

Figure 3. Cyclic voltammograms obtained at a scan rate of 50 mV s^{-1} for reduction of 2.6 mM solutions of 4-iodoanisole (curve A) and 4-bromoanisole (curve B) at a glassy carbon electrode (area = 0.077 cm^2) in dimethylformamide containing 0.1 M tetramethylammonium perchlorate.

Cyclic Voltammetric Behavior of 4-Iodo- and 4-Bromoanisole at Glassy Carbon. Figure 3 presents typical cyclic voltammograms for reduction of 2.6 mM solutions of 4-iodo- and 4-bromoanisole at a vitreous (glassy) carbon electrode in dimethylformamide containing 0.1 M tetramethylammonium perchlorate. These voltammograms, recorded at a scan rate of 50 mV s^{-1}, show single irreversible waves with peak potentials of −1.37 and −1.77 V, respectively, for 4-iodo- and 4-bromoanisole. Note that the reduction of each compound proceeds with greater difficulty at a carbon electrode than at a mercury cathode. In contrast to the cyclic voltammetric behavior of 4-iodoanisole at a mercury electrode, there is no evidence that any adsorption process takes place at glassy carbon. An examination of the relationship between peak current and scan rate for concentrations of the 4-haloanisoles ranging from 1 to 5 mM revealed that $i_p/v^{1/2}C$ is essentially constant for scan rates between 20 and 200 mV s^{-1}; in addition, the peak potential shifted negatively by approximately 80 to 110 mV for a 10-fold increase in scan rate. Thus, our observations indicate that the electrochemical reductions of 4-iodo- and 4-bromoanisole at a carbon surface both involve an uncomplicated, irreversible two-electron cleavage of the carbon-halogen bond.

Chronoamperometric Behavior of 4-Iodo- and 4-Bromoanisole at Mercury and Carbon. Single-potential-step chronoamperometric experiments were performed with both hanging mercury drop and glassy carbon electrodes to obtain more information about the electrochemistry of 4-iodo- and 4-bromoanisole in dimethylformamide containing 0.1 M tetramethylammonium perchlorate. Because diffusion coefficients for the 4-haloanisoles were unknown prior to this work, it was necessary to obtain values for these parameters. Current–time data were collected for the reduction of 2.5 mM solutions of the two starting materials at a glassy carbon electrode; the potential was stepped from −0.8 to −1.6 V for 4-iodoanisole and from −1.2 to −2.0 V for 4-bromoanisole. On the basis of the previously described cyclic voltammetric characteristics of the 4-haloanisoles, as well as their large-scale electrolytic behavior described below, it is clear that these compounds undergo two-electron reductions at carbon. Accordingly, we used an *n* value of 2 in the Cottrell equation[41] to cal-

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Table I. Coulometric Data and Product Distributions for Reduction of 4-Haloanisoles at Mercury in Dimethylformamide Containing 0.1 M Tetramethylammonium Perchlorate

			prodct distrbtn, %	
concntrtn of RX, mM	potntl, V	*n*	anisole	bis(*p*-anisyl)-mercury
RI, 2.5	−0.90	1.55	63	28
RI, 5.0	−0.90		64	33
RI, 5.2	−1.05	1.59	67	35
RI, 5.2	−1.05	1.59	70	28
RI, 5.0	−1.40	1.77	85	14
RI, 5.1	−1.40	1.79	80	15
RI, 4.6	−1.70	1.99	97	
RBr, 5.0	−1.40	2.01	101	
RBr, 2.5	−1.50	2.05	94	

Table II. Coulometric Data and Product Distributions for Reduction of 4-Haloanisoles at Carbon in Dimethylformamide Containing 0.1 M Tetramethylammonium Perchlorate

concntrtn of RX, mM	potntl, V	*n*	yield of anisole, %
RI, 2.8	−1.40	1.99	97
RI, 3.8	−1.40	2.03	101
RBr, 2.6	−1.60	2.01	99
RBr, 2.6	−1.60	1.98	96

culate diffusion coefficients of 9.2×10^{-6} and 2.0×10^{-5} cm^2 s^{-1}, respectively, for 4-iodo- and 4-bromoanisole.

In carrying out chronoamperometric measurements with a hanging mercury drop, we used the same solutions of the 4-haloanisoles mentioned in the preceding paragraph; the potential was stepped from −0.6 to −1.5 V for 4-iodoanisole and from −0.8 to −1.8 V for 4-bromoanisole. Using the experimentally obtained current–time data, together with the previously determined diffusion coefficients, we found from the Cottrell equation that, at a mercury cathode, the reductions of 4-iodoanisole at −1.5 V and of 4-bromoanisole at −1.8 V are both essentially two-electron processes resulting in the production of the *p*-anisyl carbanion.

Controlled-Potential Electrolyses of 4-Iodo- and 4-Bromoanisole. Summarized in Tables I and II are the results of controlled-potential electrolyses of 4-iodo- and 4-bromoanisole at mercury and carbon cathodes in dimethylformamide containing 0.1 M tetramethylammonium perchlorate.

For reduction of 4-iodoanisole at mercury (Table I), we selected potentials positive of the cyclic voltammetric peak potential (−0.90 and −1.05 V) and well beyond the peak potential (−1.40 and −1.70 V). For experiments conducted at −0.90 V, the reduction of 4-iodoanisole proceeds very slowly (2–3 h), and it is difficult to judge when to terminate an electrolysis; consequently, because varying amounts of starting material remain unelectrolyzed, we have chosen to base the yields of the two products on the quantity of 4-iodoanisole actually reduced. For two electrolyses listed in Table I, the sum of the yields of the products exceeds 100% slightly; this discrepancy is caused by small uncertainties in the experimentally determined peak areas and response factors used in the gas chromatographic analyses. Obviously, the distribution of products obtained upon reduction of 4-iodoanisole at mercury depends on potential; as the potential is made more negative, the yield of anisole increases whereas the quantity of bis(*p*-anisyl)mercury decreases, but 4,4′-bianisyl was never detected as a product in any experiment. In addition, the coulometric *n* value increases as the potential becomes more negative. On the basis of the coulometric data and the product distributions, we conclude that reduction of 4-iodoanisole at mercury involves a combination of one- and two-electron processes and that two-electron cleavage of the carbon–iodine bond becomes more important as the potential is made more negative.

For the electrolysis of 4-bromoanisole at mercury (Table I), the coulometric *n* value is 2 and anisole is the sole product. At the more negative potentials required to reduce the carbon–bromine bond of 4-bromoanisole, there is little chance that an electrogenerated *p*-anisyl radical intermediate will persist long enough, before accepting another electron, to interact with mercury; furthermore, bis(*p*-anisyl)mercury is itself reducible[42] at potentials where 4-bromoanisole undergoes reduction.

As revealed by the data in Table II, electrolytic reduction of 4-iodo- and 4-bromoanisole at a reticulated vitreous carbon cathode appears to be an uncomplicated two-electron process that gives rise to just one product, namely anisole.

Mechanistic Aspects of the Reduction of 4-Haloanisoles. It is reasonable to assert that the first step in the reduction of a 4-haloanisole is uptake of a single electron to form a transient radical-anion that undergoes carbon–halogen bond scission to give a *p*-anisyl radical:

$$\mathrm{CH_3OC_6H_4X} + e^- \rightleftharpoons [\mathrm{CH_3OC_6H_4X}]^{\bullet -} \xrightarrow{k} \mathrm{CH_3OC_6H_4}^{\bullet} + \mathrm{X}^- \quad (1)$$

Work by Savéant and co-workers[10] suggests that the lifetime of the radical-anion, $[\mathrm{CH_3OC_6H_4X}]^{\bullet -}$, is shorter than 100 μs, so the first electron-transfer process will appear to be irreversible at cyclic voltammetric scan rates less than approximately 10 000 V s^{-1}.

To account for the formation of anisole and bis(*p*-anisyl)mercury when 4-iodoanisole is reduced at a mercury cathode, we propose two reaction pathways involving *p*-anisyl radicals. First, the radical can accept another electron to form the *p*-anisyl anion, and the latter can be protonated to yield anisole:

$$\mathrm{CH_3OC_6H_4}^{\bullet} + e^- \rightarrow \mathrm{CH_3OC_6H_4}^- \xrightarrow{\mathrm{H^+}} \mathrm{CH_3OC_6H_5} \quad (2)$$

Although the majority of the anisole should arise from protonation of the anion by adventitious water (typically present in dimethylformamide at a concentration of 15–25 mM), the tetramethylammonium cation can serve as a proton donor.[22,31] Second, the *p*-anisyl radical can be adsorbed onto the mercury surface and can be converted into an adsorbed *p*-anisylmercury radical; the latter species quickly disproportionates into elemental mercury and bis(*p*-anisyl)mercury:

$$2\mathrm{CH_3OC_6H_4}^{\bullet} + 2\mathrm{Hg} \rightarrow 2\mathrm{CH_3OC_6H_4Hg}^{\bullet}(\mathrm{ads}) \xrightarrow{k'} [\mathrm{CH_3OC_6H_4}]_2\mathrm{Hg} + \mathrm{Hg} \quad (3)$$

According to Kashin and collaborators,[43] the lifetime of an adsorbed arylmercury radical is 100–200 μs.

Formation of bis(*p*-anisyl)mercury as a product of the electrolysis of 4-iodoanisole at mercury necessarily implies the existence of adsorbed *p*-anisylmercury radicals; consequently, one-electron reduction of such an adsorbed radical to yield elemental mercury and the *p*-anisyl anion (which subsequently gains a proton) could provide an

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alternate route to anisole. This process is analogous to one of the reactions invoked to explain the electrochemical behavior of decyl mercuric halides in dimethylformamide,[37] but this pathway to anisole is neither excluded nor required by any experimental finding in the present study. In addition, it is conceivable that the *p*-anisyl radical might abstract a hydrogen atom from the solvent to yield anisole. However, in two earlier papers from our laboratory, it was found that isobutane (obtained from *tert*-butyl radicals electrogenerated at mercury from *tert*-butyl bromide)[23] and that octane (derived from *sec*-octyl radicals electrogenerated at mercury from 2-iodooctane)[34] are both formed almost exclusively via radical disproportionation and not by abstraction of a hydrogen atom from dimethylformamide. We infer from these results that transfer of a hydrogen atom from dimethylformamide to a *p*-anisyl radical does not play a significant role in the electrochemical reduction of 4-haloanisoles.

Because reduction of 4-bromoanisole at mercury requires a potential 400–500 mV more negative than that needed to electrolyze 4-iodoanisole, the transient *p*-anisyl radical should immediately accept another electron, without the need for interaction with the surface of the mercury cathode, to give the *p*-anisyl carbanion, protonation of which affords anisole. Accordingly, we conclude that reactions 1 and 2, formulated above, account satisfactorily for the electrochemistry of 4-bromoanisole at mercury as well as for the electrochemical behavior of both of the 4-haloanisoles at carbon.

Registry No. 4-Iodoanisole, 696-62-8; 4-bromoanisole, 104-92-7.

Electrochemical Oxidation of Ketone Acylhydrazones and Their HCN Adducts in NaCN–MeOH. Transformation of Ketones to Nitriles

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A variety of aliphatic and alicyclic ketone acylhydrazones ($R_1R_2C{=}NNHCOR_3$) were subjected to electrolytic oxidation in methanol containing sodium cyanide by using a carbon anode at room temperature. The hydrazones underwent an addition of hydrogen cyanide, followed by anodic oxidation to give nitriles (R_1R_2CHCN) and methyl esters ($MeOCOR_3$), liberating N_2. This electrolytic reaction was developed into a practical procedure for the preparation of nitriles, which involves an in situ formation of HCN adducts of hydrazones ($R_1R_2C(CN)NHNHCOR_3$), prior to passing current. When the HCN adducts were prepared separately and electrooxidized under similar conditions, higher yields of nitriles could be obtained.

The electrooxidative behavior of hydrazine derivatives has been extensively studied, and it has been found that the 1,2-disubstituted hydrazines and hydrazones give the corresponding diazene or diazenium compounds in many cases, by a two-electron oxidation.[1] Several reports are available for the application of these reactive species generated anodically to organic syntheses,[2] but there are only a few reports for the synthetic application of the electrolytic oxidation of ketone acylhydrazones and related compounds.[3]

In our continued investigation of the electrochemical oxidation of nitrogen-containing compounds,[4] we were led to the oxidation of these compounds since they were expected to undergo nucleophilic reaction with anionic species at the carbon atom of the azomethine and/or the carbonyl group.

Table I. Electrolytic Oxidation of Ketone Acylhydrazones in NaCN–MeOH[a]

hydrazone	$E_{1/2}$, V vs SCE[b]	yield of nitrile,[c] %	yield of ester,[c] %
1a	0.78	70	62
1b	0.85	45	43
1c	0.85	44	45
1d	–	30	31
1e	0.86	61	64
1f	0.90	44	51
1g	0.90	27	28
2a	1.08–1.10[d]	68	
2b	1.08–1.10[d]	14	
2c	<1.10	27	
2d	–	27	
3a	0.97	61	52
3b	0.98–1.02[d]	6	
3c	<1.10	34	
3d	–	21	

[a] Anolyte: hydrazone (40 mmol) and NaCN (80 mmol) in MeOH (80 mL). Constant current: 0.5 A. Current passed: 2.2 F/mol. Temperature: ca. 17 °C. [b] Read from the current–potential curve. The measurements were carried out in 0.1 M NaCN–MeOH with Pt electrodes. The concentration of hydrazone was 2 mM and the scan rate was 0.1 V/s. [c] By GLC analysis. [d] Estimated value. The i-E curve did exhibit a well-defined S-shape, due to the closeness to that of the background.

The present paper describes the results of the electrolytic oxidation of ketone acylhydrazones and their HCN adducts in methanol-containing sodium cyanide, which can

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