

The Electroreduction of Quaternary Ammonium Compounds

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Thus dividing slope by intercept (Fig. 3) and converting to the proper units gives k_5/k_4 . Murad⁷ has shown this form of relationship to be valid also at 3020 and 2970 Å. $k_5/k_4 = 1.03 \times 10^6$ ml. mole⁻¹. The data do not permit the evaluation of k_5 and k_4 independently.

If the singlet emission efficiency at 3130 Å., 200 mm. pressure, is 1.63×10^{-3} , ϕ_3 is found to be 0.17.

From equation 19 and with the realization that $\phi_3 = 0$ at 3340 Å. one may state

$$\lim_{P_{AcH} \rightarrow 0} Q_I^{3130}/Q_I^{3340} = (1 - \phi_3)$$

$$\frac{1.80 \times 10^{-3}}{2.14 \times 10^{-3}} = 0.84$$

$$\phi_3 = 0.16$$

It should be noted that the sum of quantum yields of methane and methyl iodide in Blacet's work⁵ should be ϕ^I provided iodine does not deactivate the singlet state at the pressures used. This is almost certain to be true. This sum is about 0.2. If one calculated ϕ_4 from the rate constants at 200 mm. pressure, one obtains 0.07. Thus the total primary yield from the singlet state should be about 0.23 in satisfactory agreement with Blacet's work.

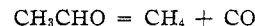
(c) 2537 Å.—At 2537 Å. emission from acetaldehyde is extremely weak but it is definitely not zero. Little can be deduced from this fact except that $\phi_3 + \phi_4$ must be nearly unity.

The quantum yield of methane formation in the presence of 12 or more millimeters of nitric oxide is about 0.65 and is somewhat pressure dependent but temperature independent. In Blacet's⁵ work, iodine suppresses about one-half of the methane formation. Blacet's methyl iodide yield is about 0.38, independent of temperature. Pressure dependence was not studied. Thus

the primary yield is about unity and comes entirely from the singlet state at this wave length.

One may conclude, therefore, that iodine suppresses part but not all of the non-free radical methane formation and does not suppress radical formation by (1a). The radical formation is presumably all by (3).

One could speculate on the kind of intermediate complex which would lead to non-free radical methane and carbon monoxide formation. The change in enthalpy for



is small. Methane behaves in many ways as an inert gas so that one would expect a repulsion between the two product molecules. Insertion of the aldehyde hydrogen between the two carbon atoms by a combination of carbon-carbon stretching and carbon-hydrogen bending motions might lead to the right result. Unfortunately there is little one can deduce from the spectrum along these lines. One may make the following statements:

1. At all wave lengths emission is a minor means of energy dissipation in acetaldehyde.
2. Dissociation at 3340 Å. must be mainly if not exclusively from the triplet state. Triplet emission at this wave length is only about one-third the intensity of the singlet emission.
3. Dissociation at 3130 Å. arises apparently from two sources: (a) a rapid process possibly arising from an upper repulsive state; (b) a somewhat slower process from vibrationally excited singlet state molecules. There is also some temperature dependent triplet dissociation at this wave length.
4. Dissociation at 2537 Å. must occur almost exclusively from the singlet state and emission is very weak.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF TEXAS, AUSTIN, TEX.]

The Electroreduction of Quaternary Ammonium Compounds¹

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The electroreduction of anilinium chloride (AC), dimethylanilinium chloride (DMAC) and benzyldimethylanilinium bromide (BDAB) was studied polarographically and coulometrically. Analysis for the reduction products was performed spectrophotometrically. Application of Koutecký's treatment for irreversible polarographic waves indicated that all of the reductions involved a one-electron rate-determining step. Coulometry of AC and DMAC showed that one electron was also consumed in the over-all reaction. For BDAB, however, the apparent number of faradays per mole, n_{app}^0 , for the coulometric reduction in water, acetonitrile and N,N-dimethylformamide varied between 1.4 and 2.0. A mechanism for this reduction involving primary formation of a benzyl free radical, which either reacts with the solvent or couples, is proposed. Reduction of BDAB in the microwave cavity of an electron paramagnetic resonance spectrometer provides further evidence of a free radical intermediate.

The mechanism of the electroreduction of quaternary ammonium compounds has been the subject of several recent studies. Finkelstein, Peterson and Ross³ carried out uncontrolled, macroelectrolyses of several substituted anilinium salts at platinum and aluminum cathodes. Southworth, Osteryoung, Fleischer and Nachod⁴ recently reviewed the past literature and examined the polarographic and macroelectrolytic reduction of a number of aliphatic and aromatic quaternary ammonium compounds. Both groups, on the

basis of the nature of the products obtained, postulated an initial one-electron electrode reaction. Definitive electrochemical evidence for this reaction scheme was lacking, however. The present study was undertaken to obtain this evidence and to apply controlled potential coulometry, a technique which has proved very useful for the elucidation of electrode mechanisms,⁵ to a study of this reaction. Substituted anilinium compounds, which produce the best-defined polarographic waves and reduce well before the discharge of the supporting electrolyte, were chosen as model compounds in this study.

Results and Discussion

Polarography.—Well defined, irreversible, polarographic waves were obtained for the reduction of ani-

(1) (a) Based on a thesis submitted by J. S. Mayell in partial fulfillment of the requirements for the degree of Ph.D., June, 1962. (b) Presented at the 140th National Meeting of the American Chemical Society, Chicago, Ill., September, 1961.

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(3) M. Finkelstein, R. C. Peterson and S. D. Ross, *J. Am. Chem. Soc.*, **81**, 2361 (1959); **82**, 1582 (1960).

(4) B. C. Southworth, R. Osteryoung, K. D. Fleischer and F. C. Nachod, *Anal. Chem.*, **33**, 208 (1961).

(5) (a) D. H. Geske and A. J. Bard, *J. Phys. Chem.*, **63**, 1057 (1959); D. H. Geske, *ibid.*, **63**, 1062 (1959); (b) S. Karp and L. Meites, *J. Am. Chem. Soc.*, **84**, 906 (1962).

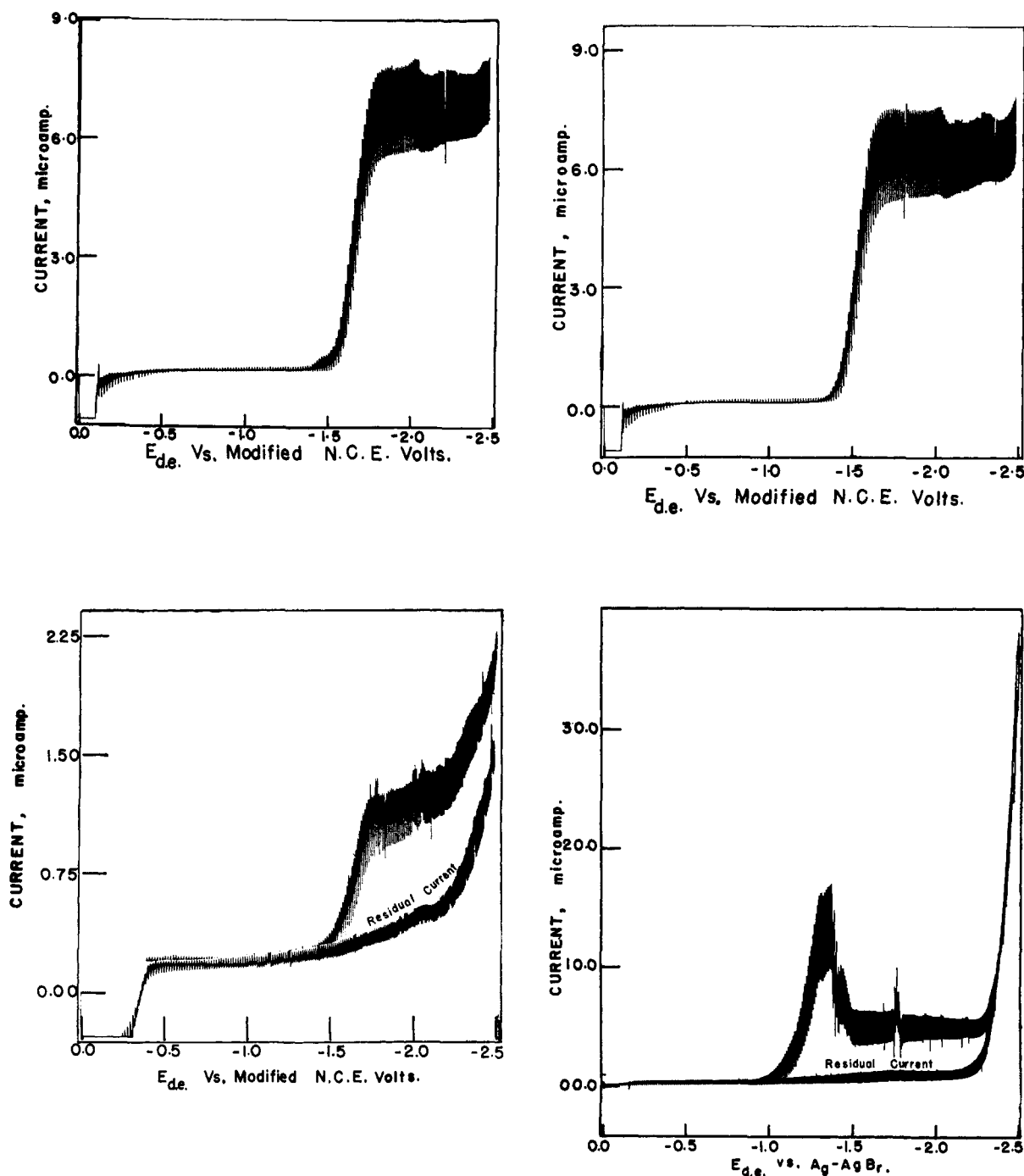


Fig. 1.—Typical polarograms for the reduction of quaternary ammonium compounds: upper left, 1.50 mM AC in 0.1 M tetrabutylammonium bromide; upper right, 1.30 mM DMAC in 0.1 M tetrabutylammonium bromide; lower left, 0.125 mM BDAB in 0.1 M tetraethylammonium hydroxide; lower right, 0.50 mM BDAB in 0.1 M tetrabutylammonium bromide in acetonitrile.

linium chloride (AC), dimethylanilinium chloride (DMAC) and benzyldimethylanilinium bromide (BDAB) in aqueous solutions, containing 0.1 M tetraalkylammonium salts as supporting electrolyte. A well-defined wave cannot be obtained for the reduction of trimethylanilinium chloride, which starts to reduce at a potential close to that of the supporting electrolyte. The polarographic wave of BDAB at a concentration of 0.66 mM shows a maximum which is suppressed by the addition of 0.0057% gelatin. Reducing the BDAB concentration to 0.125 mM also resulted in the disappearance of the maximum. BDAB also produced well-defined waves in acetonitrile and *N,N*-dimethylformamide, using 0.1 M tetrabutylammonium bromide as a supporting electrolyte. The maxima observed

TABLE I
POLAROGRAPHIC RESULTS FOR REDUCTION OF QUATERNARY AMMONIUM COMPOUNDS AT 25°

Compound	Solv.	I^a	$-E_{1/2}$, v. vs. N.H.E.	η_a^b
AC	H ₂ O ^c	3.24	1.36	1.06
DMAC	H ₂ O ^c	3.43	1.23	1.06
BDAB	H ₂ O ^d	4.49 ^e	1.33	1.07
BDAB	H ₂ O ^{d,e}	3.52	1.27	..
BDAB	CH ₃ CN ^c	6.29	1.11 ^f	..

^a $I = i_a/Cm^{1/2}/v^{1/2}$. ^b Assuming $\alpha = 0.50$. ^c 0.1 M tetrabutylammonium bromide. ^d Tetraethylammonium hydroxide. ^e 0.0057% gelatin added. ^f v. vs. silver wire immersed in 0.1 M tetrabutylammonium bromide in CH₃CN. ^g No maximum observed at concentrations of 0.125 mM or below.

TABLE II
 CONTROLLED POTENTIAL COULOMETRIC RESULTS

The supporting electrolyte was tetrabutylammonium bromide; the cathode was mercury and the anode was silver; the temperature was 25°; DMA = N,N-dimethylaniline, DMF = N,N-dimethylformamide

Cmpd.	Solv.	Contr. pot., v. vs.	Initial	Initial	n_{app}^0	Products
		M.N.C.E.	concn., mM	current, ma.		
AC	H ₂ O	-2.00	1.9	55	0.98	Aniline, (H ₂)
DMAC	H ₂ O	-2.00	2.2	51	0.93	DMA, (H ₂)
BDAB	H ₂ O ^a	-1.90	1.25	83	2.00	DMA, toluene
BDAB	N ₂ O ^a	-1.90	1.5	90	1.96	DMA, toluene
BDAB	N ₂ O ^a	-1.90	2.5	121	1.97	DMA, toluene
BDAB	CH ₃ CN	-1.70 ^b	1.25	93	1.94	DMA, toluene
BDAB	CH ₃ CN ^c	-1.70 ^b	16.90	318	1.86	DMA, toluene, bibenzyl
BDAB	CH ₃ CN ^d	-1.70 ^b	1.00	39	1.66	DMA, toluene, bibenzyl
BDAB	CH ₃ CN ^d	-1.70 ^b	17.10	260	1.40	DMA, toluene, bibenzyl
BDAB	DMF	-1.70 ^{b,e}	0.125	4	1.95	DMA, toluene
BDAB	DMF	-1.70 ^{b,e}	5.14	450	2.01	DMA, toluene

^a Supporting electrolyte was tetraethylammonium hydroxide and anode was platinum. ^b v. vs. silver/silver bromide. ^c Temperature was 0°. ^d Temperature was -35°. ^e The electrolysis was performed in the dark.

on the waves in these solutions could not be suppressed by the usual polarographic maxima suppressors. Typical polarograms are shown in Fig. 1 and a summary of the polarographic data is given in Table I.

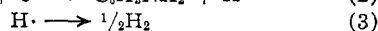
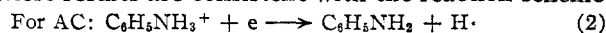
The polarographic current-potential curves were analyzed by the treatment of Koutecký,⁶ assuming that the reductions were totally irreversible. From the ratios of the instantaneous currents i/i_d , the parameter λ , was calculated. (The symbols used are defined by Delahay.⁷) From λ , which is defined as

$$\lambda = k_{t,h} t^{1/2} / D_0^{1/2} \quad (1)$$

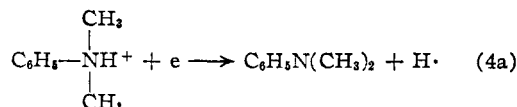
and diffusion coefficients obtained from the limiting currents (assuming the total number of electrons consumed in the process n , was that determined by controlled potential coulometry), $k_{t,h}$ was calculated. The plots of $\log k_{t,h}$ vs. potential were linear in all cases, and from the slopes, given by $\alpha n_a F / RT$,⁷ αn_a was calculated. Values of n_a for the polarographic reductions, assuming α was about 0.5, are shown in Table I: Note that for all of the reductions n_a is close to one. The linearity of the $\log k_{t,h}$ -potential plots provides evidence that there is only a single rate-determining step, involving n_a electrons, perhaps followed by more rapid reactions involving $n - n_a$ electrons.

Controlled Potential Coulometry.—Results obtained for the controlled potential coulometric reduction of AC, DMAC and BDAB under various conditions and in several solvents is shown in Table II. Electrolysis products were usually determined by ultraviolet spectrophotometry, although infrared spectrophotometry and vapor phase chromatography were also employed for product identification.

AC and DMAC.—Controlled potential coulometric electrolysis indicates that one faraday of electricity is consumed per mole of reactant in the over-all reaction. A gas, presumably hydrogen, was evolved during the reductions. The yields of the reduction products, aniline and dimethylaniline, for the electrolysis of AC and DMAC, respectively, were essentially quantitative. These results are consistent with the reaction scheme



For DMAC:

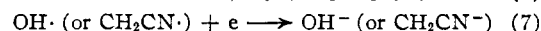
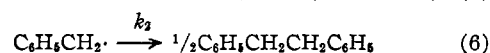
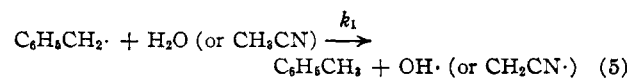
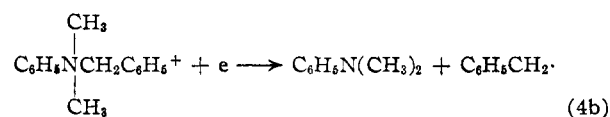


followed by reaction 3.

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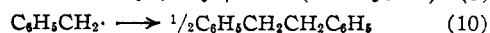
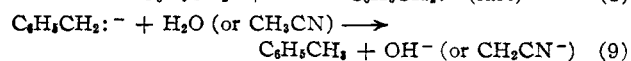
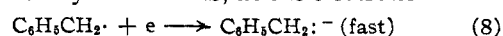
BDAB.—Coulometric data for the reduction of BDAB show that, at 25° in water, acetonitrile and N,N-dimethylformamide, two faradays are consumed per mole of BDAB in the over-all reaction, although the rate-determining electrode reaction involves only one electron. In all of the electrolyses of BDAB the yield of dimethylaniline was quantitative. A reaction scheme consistent with these results is



If reaction 6 predominated, coulometric data would indicate only one faraday consumed per mole in the over-all reaction, while if reaction 5 predominated, two faradays per mole could be consumed. Under conditions where both 5 and 6 are important, n_{app}^0 varies between one and two. At lower temperatures reaction 6 should become relatively more important because its activation energy is probably smaller than that of 5. Results in acetonitrile at 0° and -35° confirm this prediction. Moreover, reaction 6, being second order in benzyl radical, should be favored by higher initial concentrations of starting material (compare results in acetonitrile at -35° for initial concentrations of 1.00 and 17.1 mM).

In solutions where n_{app}^0 was near two, only toluene was found as a reaction product. When n_{app}^0 was less than two both toluene and bibenzyl were observed. Figure 2 shows ultraviolet spectra of samples obtained by extraction of the electrolyzed solution with *n*-hexane. Note the peak at 266 m μ , which is characteristic of bibenzyl, that is present in the spectra obtained during the electrolysis of the 17.0 mM BDAB solution at -35° in acetonitrile.

Alternate Mechanisms.—Several other reaction schemes which will satisfy the experimental evidence can be written. One involves reduction of the benzyl radical formed by reaction 4b, at the electrode



This scheme seems less probable than the preceding one because, if benzyl radical was reduced directly at the

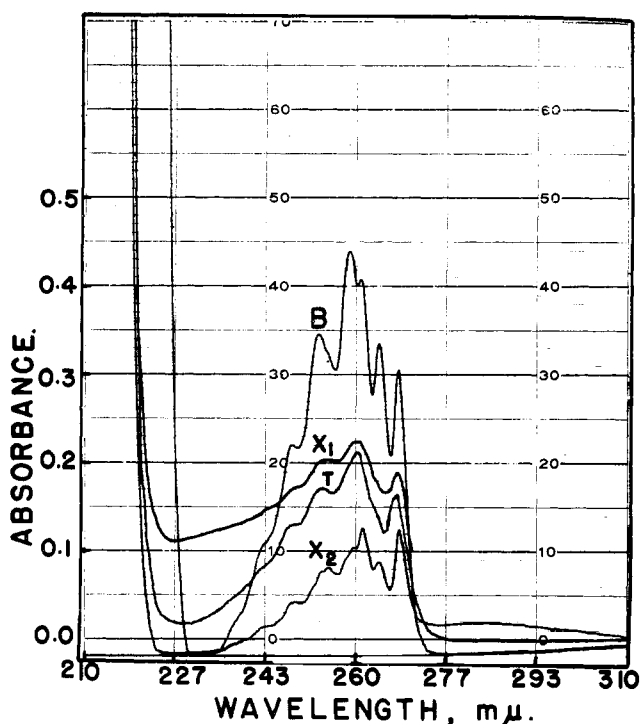
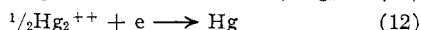
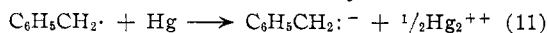


Fig. 2.—Ultraviolet spectra of: T, 1 mM toluene in *n*-hexane; B, 1.0 mM bibenzyl in *n*-hexane; X₁, *n*-hexane extract of electrolyzed acetonitrile solution initially containing 1.25 mM BDAB; X₂, *n*-hexane extract of electrolyzed acetonitrile solution initially containing 17.0 mM BDAB (−35°).

electrode surface, there would probably be very little opportunity for radical coupling to occur, and n_{app}^0 values of less than two would not be obtained.

The benzyl radical formed by the initial electrode reaction could react with the mercury



and reactions 9 and 10. The intervening reactions may occur through the formation of dibenzylmercury. The net result of this reaction scheme is the same as that of the proposed scheme, but replaces the reaction of the radical with the solvent with a reaction with mercury. The formation of colloidal mercury was observed during the electrolysis of higher concentrations of BDAB, which might lend some support to this mechanism. However, colloidal mercury formation is also found during reduction of simpler quaternary ammonium compounds⁴ and has been identified as the breaking down of intermediately formed quaternary ammonium amalgams.

The abstraction of hydrogen from a solvent by a free radical is a well-known type of reaction. Hickinbottom⁸ demonstrated that benzyl radicals, formed by the reaction of phenyl benzyl ether with copper, reacted with the solvent quinoline and formed toluene. Although the reaction in acetonitrile may involve reaction of the radical with small amounts of water inevitably present, reaction between the radical and the acetonitrile is also possible. Wijnen⁹ found that deuterated methyl radical abstracted hydrogen from acetonitrile and formed CD₃H. When considering the relative probability of radical dimerization, the principle of the "cage effect"¹⁰ is usually applied. The usual methods of forming free radicals, such as thermal decomposition or photochemical dissociation, lead to

the production of pairs of radicals. These radicals, held near one another by a cage of solvent molecules, have a greater probability of combining than they would have if they diffused into the bulk of the solution. In the electrolytic formation of free radicals the cage effect leads to a different behavior, since only one radical at a time is produced at a given location on the electrode surface. The cage of solvent molecules prevents the diffusion of one radical to another, and only when the radical density at the electrode surface is high (*i.e.*, high current density) does the dimerization reaction become probable. Two-dimensional diffusion of electrogenerated radicals along the electrode surface, with subsequent combination, may also occur.

Electron Paramagnetic Resonance Spectrum.—Geske and Maki¹¹ demonstrated that electron paramagnetic resonance (e.p.r.) spectroscopy is a useful technique for detecting electrogenerated free radicals. When the electroreduction of a 10 mM BDAB, 0.2 M tetrabutylammonium bromide, acetonitrile solution at *ca.* −35° was performed inside the microwave cavity of an e.p.r. spectrometer, a signal was obtained. With an electrolysis current of 20 μamp. the potential of the mercury pool electrode was about −1.60 v., and a spectrum with a good signal-to-noise ratio was obtained after about four hours. The spectrum showed an incompletely resolved triplet with relative intensities of about 1:2:1. The total width of the spectrum measured between centers of the two extreme components was 12.5 gauss; the width of the central peak was about 3.2 gauss. The spectroscopic splitting factor was, as usual, near the free electron *g*-value. That the observed signal was due to an electrogenerated radical was demonstrated by turning off the electrolysis current while tracing the e.p.r. absorption at a magnetic field fixed at one peak of the spectrum. The resulting trace showed a drop in the signal to the noise level in about 45 seconds. This time interval is chiefly associated with the relaxation time of the spectrometer rather than with the lifetime of the radical, which we think is much shorter. No e.p.r. spectra were obtained with acetonitrile solutions containing only supporting electrolyte. Since the electrogenerated radical is destroyed by both reaction with the solvent and coupling, the steady state concentration of the radical is quite small, and is highest near the electrode surface. Spectra were not obtained at room temperature, probably because of the high rate of radical destruction under these conditions.

It has been difficult to reproduce the results of the e.p.r. experiment. Difficulties stem from problems of cooling, orientation of the mercury electrode, tuning of the spectrometer, etc., so that a fortuitous set of conditions may be necessary to observe a signal of sufficient amplitude to be above the noise level. Good spectra were obtained twice out of ten attempts at different conditions. The very presence of an e.p.r. signal is persuasive evidence of a one-electron, radical-forming mechanism, and makes the reaction scheme involving addition of an electron directly to the benzyl radical unlikely.

Rates of Secondary Reactions.—Controlled potential coulometric data can be used to estimate rate constants of secondary reactions.^{5a} A theoretical treatment of the type of reaction scheme proposed here was performed by Bard and Mayell.¹² The experimental values of n_{app}^0 obtained in acetonitrile at −35° fit theoretical n_{app}^0 vs. concentration curves, and suggest a ratio of k_1'/k_2 of about 10^{−3} (where k_1' is the pseudo first-order rate constant of reaction 5, and k_2 is the second-order

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rate constant of reaction 6). This ratio may be significantly in error if both k_1' and k_2 are very large, because most of the secondary chemical reaction would then occur very close to the electrode surface, and the homogeneous concentration of intermediate assumed in the theoretical model would not be obtained.

Conclusions.—The type of reaction mechanism observed in this case is probably common to many organic electrode reactions, and it may be fruitful to venture some general conclusions concerning how different electrolysis conditions may effect the path of the over-all reaction and the yields of the products. The potential, not the current density, is usually assumed to be the primary factor determining the course of an electrode reaction. However when competitive first- and second-order secondary reactions occur, the current density (which is related for constant potential electrolysis to the initial concentration of the electroactive species) becomes a factor in determining the path of the over-all electrode process. At low current densities the first-order reactions predominate, while at high current densities second-order reactions become more important. The primary charge-transfer step, as opposed to the over-all electrode reaction, as usual, is primarily potential dependent. This study also suggests that temperature is an important variable governing the over-all reaction path. Decreasing the temperature will favor secondary reactions with relatively low activation energies (such as radical coupling reactions). The solvent is also important in determining the nature of the products obtained, especially when it itself is involved in a secondary reaction. For example, the free radical concentration and the yield of dimer would probably have been increased if toluene was used as a solvent, since the reaction of benzyl radical with toluene would merely regenerate the radical. Unfortunately, toluene has a low dielectric constant and most supporting electrolytes and BDAB were not soluble in it.

Experimental

Reagents.—AC, DMAC and BDAB were prepared by refluxing the amine and the halide in benzene, ether and acetone, respectively. Trimethylammonium chloride was obtained from Eastman Kodak Co. All were purified by recrystallization, three times, from ethanol-ether mixtures. Acetonitrile and N,N-dimethylformamide were Matheson, Coleman and Bell Spectro Grade and were used as obtained. Tetrabutylammonium bromide and tetraethylammonium hydroxide were obtained from Southwestern Analytical Chemicals, and were of Polarographic Grade.

Polarographic Apparatus.—Polarograms were recorded on a Sargent Model XXI recording polarograph. The dropping mercury electrode (D.M.E.), incorporating a Sargent S-29419 capillary, had a value of $m^2/t^{1/2}$ of about 1.53 mg.^{2/3} sec.^{1/3} in aqueous solutions at about -2.0 v. vs. M.N.C.E. The all-glass polarographic cell was equipped with inlets for the D.M.E., the reference electrode and nitrogen. All measurements were made at 25.00 ± 0.05°. The reference electrode for aqueous solutions was a modified normal calomel electrode (M.N.C.E.) in which

1.0 M tetramethylammonium chloride was used in place of the usual 1.0 M potassium chloride. The reference electrode was separated from the sample solution by a sintered-glass disk and an agar plug. For non-aqueous solvents, the reference electrode, a silver wire immersed in 0.10 M tetrabutylammonium bromide, was separated from the sample solution by two sintered-glass disks.

Controlled Potential Coulometry.—A rapid response potentiostat, similar to that available commercially from Elektronische Werkstätten, Gottingen, Germany, was used for most of the electrolysis. For trials involving higher concentrations of the quaternary ammonium compound an electromechanical potentiostat, similar to the one described by Lamphere,¹⁸ was employed. Current-time curves were recorded on a Sargent SR recorder equipped with a Disk Instrument Company integrator. The electrolysis cell was an all-glass H-cell; the cathode and anode compartments were separated by a 3-cm. diameter sintered-glass disk and frequently a pure agar plug on the anode compartment side. The cathode, a mercury pool with a 50 cm.² area, could be introduced and removed through the bottom of the cell. The anode was a silver wire, except for reduction of BDAB in an aqueous 0.1 M tetraethylammonium hydroxide solution, when a platinum foil auxiliary electrode was used. The resistance between the anode and cathode in this cell was between 100 and 200 ohms. The reference electrodes were the same type as those used for polarography.

All solutions were deaerated by passing nitrogen through them prior to, and during, the electrolysis. A mechanical stirrer was used to keep the mercury-solution interface in smooth motion. The supporting electrolyte solution was first pre-electrolyzed at the appropriate control potential until the residual current decayed to a small, constant, value. The mercury pool was removed, the sample added and deaerated, the mercury re-introduced, and the electrolysis performed. The cathode potential was usually monitored with a potentiometer and second reference electrode. The electrolysis current usually decayed to background in about 1 hour. The amount of substance left unreduced after electrolysis was determined by polarography, and corrections were applied when necessary.

E.p.r.—A Varian Model 4500 e.p.r. spectrometer was employed, with the magnetic field modulated at 400 c.p.s. The technique of generation and detection was similar to that of Geske and Maki.¹¹ The electrolysis cell comprised a 3-mm. o.d. quartz tube, sealed to a jacketed Pyrex cell, held at about -35° with a Dry Ice-2-propanol mixture. The mercury pool had an area of about 0.125 cm.². The sample was subjected to a preliminary deaeration with nitrogen and was cooled by raising the mercury level so that the solution was completely within the jacket portion of the cell. The flow of nitrogen was continued during the electrolysis. The cell assembly was positioned along the axis of the microwave cavity, with the surface of the mercury pool slightly below the vertical center of the cavity.

Solution Analysis.—The electrolysis solutions were first examined by ultraviolet spectrophotometry to determine aromatic amines; aniline at 280 m μ and dimethylaniline at 243 and 299 m μ . The solutions were then treated with gaseous HCl (to convert the amine to the quaternary ammonium chloride) and extracted with ether or *n*-hexane. The ether and *n*-hexane layers were analyzed by ultraviolet and infrared spectrophotometry and vapor phase chromatography. Spectrophotometric measurements were performed with Beckman Model DK-1 and Baird Model 4-55 recording spectrophotometers. A Wilkens Instruments Model A-90-P aerograph was employed for vapor phase chromatographic analysis.

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