THACKER, JR., FRANKLIN AUBREY. A Method for the Identification of the Products from Controlled-Potential Coulometry of p-Nitrosophenol, p-Nitrophenol and p-(p-Hydroxyphenylazo)-benzenesulfonic Acid Sodium Salt. (1976) Directed by: Dr. Harvey B. Herman. Pp.44

The aim of this study was to identify the controlled-potential coulometry products after electrolytic reduction of p-nitrosophenol, p-nitrophenol, p-(p-hydroxyphenylazo)-benzenesulfonic acid sodium salt, Orange I, and Orange II. Polarography was performed on all individual compounds in two buffer solutions at pH 4.9 and 11.8 using the dropping mercury electrode polarographic circuit. The resulting polarograms were used to select the controlled working electrode potentials for coulometry.

Coulometry was conducted with the individual compounds and each pH buffer solution in a stirred mercury pool coulometry cell. The potential was controlled and the number of electrons (n) involved in the reduction process was determined with the aid of an electrical circuit whose output voltage was proportional to n.

The coulometric reaction solutions were evaporated and the product residues were treated with silylating reagent to form silyl derivatives. The silyl derivatives increased product volatilities so that identification by gas chromatography was possible.

Gas chromatography was performed using a packed glass column. The silylated coulometric product was detected by flame ionization.

As expected, the nitroso, nitro and azo compounds gave coulometric n values equal to 4, 6, and 4 respectively. Also, p-aminophenol was identified as the product after coulometry of p-nitrosophenol, p-nitrophenol, and p-(p-hydroxyphenylazo)-benzenesulfonic acid sodium salt. The coulometry products of Orange I and Orange II were not able to be identified by gas chromatography, apparently because of instability of the anticipated amino-naphthol compounds.

From the identification of the products along with the n values obtained after coulometry in pH 4.9 and 11.8 buffer solutions, reaction schemes were formulated for the electrolysis reductions of the above compounds.

A METHOD FOR THE IDENTIFICATION OF THE PRODUCTS

FROM CONTROLLED-POTENTIAL COULOMETRY OF

P-NITROSOPHENOL, P-NITROPHENOL,

P-(P-HYDROXYPHENYLAZO)BENZENE-

SULFONIC ACID SODIUM SALT

by

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APPROVAL PAGE

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INTRODUCTION

Controlled-potential coulometry emerged in the early 1940's (1,2) and since then has been used to study many electrolysis reduction and oxidation reactions of inorganic and organic compounds in solution. Numerous chemical systems which have been investigated using the controlled-potential coulometry technique are described in references (3,4) by two well-known authorities in this field of study.

In most studies polarography was used to determine the potentials where electrolysis occurs for the particular chemical system. The electrolysis potentials were controlled during the coulometry experiments.

Controlled-potential coulometry has been used in many cases to synthesize compounds (5,6) and also to elucidate the mechanism of the electrolysis.

Theory of Polarography

For electrolysis to occur, a potential difference must be impressed between two electrodes in solution. The potential difference required to cause continuous electrolysis to occur is the decomposition potential and this potential is dependent on standard electrode potentials, solution composition, and surface effects. As the voltage is increased beyond the decomposition potential, the current which flows increases continuously in ordinary electrolysis. However, as shown by Heyrovsky (7), if one electrode is a microelectrode, e.g., the dropping-mercury electrode, current versus voltage curves

are obtained whose characteristics lead to practical analytical applications.

As a continuous increase of potential difference is applied to the cell, the current will be very small until the voltage drop at the mercury drop cathode is enough to cause reduction of the compound at the lowest reduction potential. The current rapidly increases but is limited by concentration polarization at the microcathode. The rate of diffusion of the reducing reactant to the electrode and its concentration determine this limiting current if there is a large amount of supporting electrolyte and only if it is not involved in the cathode reaction.

Fresh drops of mercury are formed continuously and conditions vary during formation and release cycle of the drop but they are constant over long time periods. A theoretical equation derived by Ilkovic (8): $I_D = knD^{1/2}m^{2/3}t^{1/6}C$ where

I_D = diffusion current, amp.

k = 607 where I_D is the mean diffusion current.

n = number of electrons transferred in electrode reaction

D = diffusion coefficient of reducible species, cm^2/sec.

m = rate of mercury flow from tip, mg/sec.

t = drop time, sec.

C = concentration of reactant, millimoles/liter.

The proportionality between I_D and C is a direct consequence of the concentration polarization of the dropping-mercury electrode.

Theory of Controlled-Potential Coulometry

The theoretical basis of coulometry at controlled-potential is described by the following mathematical equation (4):

$$q = \int_0^t idt = nFN^o \text{ where}$$

q = number of coulombs of electricity consumed.

i = current in amperes after t seconds.

t = seconds required for electrolysis.

n = number of electrons involved in the electrolysis reaction.

F = number of coulombs per Faraday.

N^o = number of moles of substance electrolyzed.

Thus if q is found, then by knowing either n or N^o, the other unknown may be determined. There are certain requirements for the above equation to be valid. First, the electrolysis potential has to remain constant and secondly it is assumed that only one compound is electrolyzed at the working electrode.

The apparatus for conducting the controlled-potential coulometry experiment includes an electrolysis cell, with either a mercury pool or platinum gauze electrode, a potentiostat to control the electrolysis potential between the reference and working electrodes. The current produced is then measured with a coulometer which measures current versus time or the current area under the current-time curve is integrated to give a direct relation of number of coulombs produced during electrolysis.

The Silylation Reaction

Silylation is the addition of a trimethylsilyl group, $-Si(CH_3)_3$ on a molecule and this silyl group usually substitutes for an active hydrogen atom. There are numerous silylating reagents (9), however, there is one reagent that best suited the experimental requirements of this study. The reagent is N,O-bis(trimethylsilyl) acetamide, or for short BSA and has the following chemical structure:

$$CH_3C \overset{\displaystyle OSi(CH_3)_3}{\underset{\displaystyle NSi(CH_3)_3}{}}$$
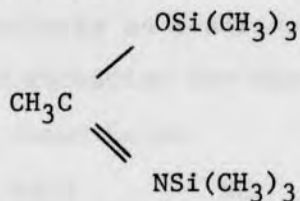
BSA reacts with both $-NH_2$ and $-OH$ groups of chemical compounds, which are groups attached to the compounds that will be involved in this study. BSA combines with $-NH_2$ and $-OH$ to form $-NHSi(CH_3)_3$ and $-OSi(CH_3)_3$ respectively. In addition, the silyl derivatives become more volatile than their unsilylated compounds allowing for analysis by gas chromatography.

Previous Work

Numerous investigators have studied the reduction by electrolysis of nitroso, nitro, and azo phenol compounds. These investigators have performed polarography and coulometry experiments in order to determine the n values for the specific reaction conditions.

A thorough investigation of the electrolytic reduction of p-nitrosophenol has been made by Alberts and Shain (10).

They studied the polarographic behavior of p-nitrosophenol
in various acid and base aqueous alcohol buffer solutions
covering a pH range of 1.7-12.1. At acidic pH values, two
polarographic waves were found while at basic pH values only
one wave was found. They also performed coulometry experiments
on p-nitrosophenol in pH 4.8 and 12.3 buffer solutions. The
total number of electrons involved in the electrolysis reduction
was equal to four. They also identified the coulometric prod-
uct spectrophotometrically as p-aminophenol. Their findings
confirmed a proposed mechanism for the electrolysis of p-nitro-
sophenol (11,12) as shown below.

$$N{=}O \xrightarrow[2H^+]{2e^-} HNOH \xrightarrow[-H_2O]{k_f} NH \xrightarrow[2H^+]{2e^-} NH_2$$
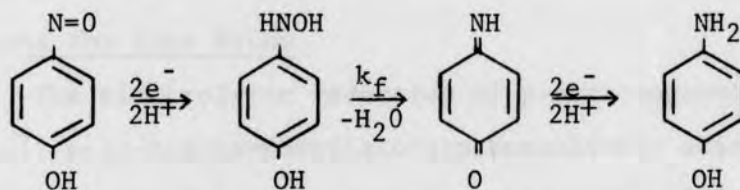
The above mechanism is also supported by the reduction of
nitrobenzene (13) which reduces to p-nitrosobenzene, then to
phenylhydroxylamine, and finally to aniline.

Lindbeck and Freund (14) studied the electrolysis re-
duction of p-nitrophenol and other nitro substituted compounds
in dimethyl sulfoxide containing 0.5M LiCl at -1.6 to -1.8
volts versus SCE and found n values equal to 4 and 6. For the
n=6, the following mechanism was proposed:

$$NO_2 \xrightarrow[4H^+]{4e^-} HNOH \xrightarrow{-H_2O} NH \xrightarrow[2H^+]{2e^-} NH_2$$
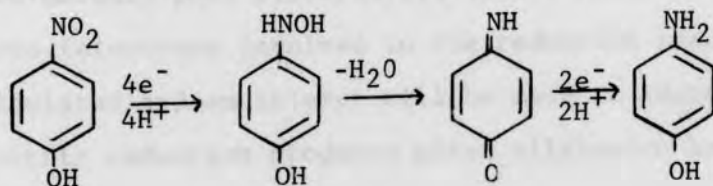
Several detailed studies on the electrolysis reductions of azo compounds have been made. Laitinen and Kneip (15) evaluated the reduction of N,N-dimethyl-p-phenylazoaniline in 50% acidic ethanol solutions and found that four electrons were involved in the reduction reaction. Florence (16,17,18) has studied the polarography of aromatic azo compounds and also conducted controlled-potential coulometry with a large pool mercury electrode. He found n values equal to 4 for the reduction of Orange I at pH values of 4, 9, and 13. For Orange II and p-(p-hydroxyphenylazo)benzenesulfonic acid he found n=4 at pH 9.

Reasons for this Study

The electrolytic reduction of p-nitrosophenol, p-nitrophenol, p-(p-hydroxyphenylazo)benzenesulfonic acid, Orange I, and Orange II will be studied for this work. Reduction of these products will be performed in acidic, pH 4.9, and basic, pH 11.8, buffer solutions. Polarography experiments will be conducted and polarograms obtained for the reduction using the dropping mercury electrode. The potentials determined from polarography are to be used in the controlled-potential experiments. Controlled-potential coulometry experiments will be done on all of the above compounds with the aid of the stirred-mercury pool electrolysis cell. After coulometry, n values (electrons involved in the reduction reaction) will be calculated and an attempt will be made to identify the coulometric reduction products after silylation by gas

chromatography. The n value in conjunction with positive identification of the coulometric products will be used in order to set up coulometric reduction equations.

EXPERIMENTAL

Preparation of Buffer Solutions

Acidic and basic buffer solutions were prepared identical
to the acid and base buffers described and used by Alberts
and Shain (10) in their electrolysis reduction study of p-nitro-
sophenol. The acid buffer was made to contain 0.1M acetic acid
and 0.1M potassium acetate. The base buffer was prepared with
0.05M disodium phosphate and 0.05M trisodium phosphate. Both
acid and base buffers also contained 20% ethanol with the ionic
strength adjusted to 0.3M with potassium nitrate. The acetic
acid and other inorganic salts used were analytical reagent
grade. Distilled, deionized water was used to prepare all
aqueous solutions.

pH Measurement of the Buffer Solutions

For pH measurement, an Orion Research Ionanalyser,
Model 801/digital pH instrument was used. The pH of a buffer
was read as millivolts by the instrument. A calibration plot
was made after Beckman pH buffer solution standards of pH
equal to 4.01, 6.86, and 9.18 were measured. A plot of
standard buffer pH versus millivolts is shown in figure 1.
As expected the plot gives a straight line. The x and y
coordinate values were inserted into a standard linear re-
gression program, LINFIT, and as a result of its calculation
pH=-0.0171mv + 6.952.

The prepared acid and base buffers were both measured
with the Ionanalyser and the millivolts reading was made.

FIGURE 1

CALIBRATION PLOT FOR BUFFER STANDARDS

The numerical values were inserted into the LINFIT computer derived formula shown above and after calculation the pH of the acid buffer and base buffer were 4.9 and 11.8 respectively.

Polarography Procedure

The Heathkit Dropping Mercury Electrode Apparatus was used for polarography experimentation. The following parameters were set and used throughout polarographic analysis:

Temperature = 25° C

Mercury Drop Rate = 1 drop per 5 seconds

Sweep Rate = 0.1 volt per minute

Damping = 3

Mercury Height = 750 mm

Prior to polarography, two drops of Triton X-100 (1% by weight) were added to the solution. Also, the solution to be analyzed was deoxygenated by bubbling nitrogen gas through the solution for fifteen minutes. Bubbling was discontinued during the polarography voltage scan.

Controlled-Potential Coulometry Apparatus

The electrolysis cell for the controlled-potential coulometry experiment was basically the mercury pool cell described in a paper by J. E. Harrar (19). The complete cell, as constructed, is shown in figure 2. The cell cap was made of teflon while the cell itself was made of 41-mm-o.d. borosilicate glass tubing that was sealed to a three-way,

FIGURE 2

ELECTROLYSIS CELL FOR COULOMETRY

STIRRER

NITROGEN GAS

TEFLON CAP

COUNTER ELECTRODE

MERCURY

PLATINUM WIRE

SATURATED CALOMEL ELECTRODE

SALT BRIDGE TUBES

COULOMETRY SOLUTION

STOPCOCK

MERCURY

teflon-plug stopcock with a 2-mm bore. A short length
(0.5 in.) of platinum wire was sealed in the glass for con-
tact with mercury.

The saturated calomel reference electrode (SCE) was
constructed by the procedure described by Meites, et al. (20).
A layer of pure mercury was placed in the tube bottom and a
few grams of mercurous chloride was added over the mercury and
finally a larger amount of potassium chloride was added.   The
tube was then filled with water saturated with potassium
chloride.

Agar was the salt bridge media. The media was made by
warming four grams of agar with 100 milliliters of water to
approximately 90° C on a steam bath until the agar was dissolved
and then 35 grams of potassium chloride was added.

The applied potential between the reference and working
electrode was controlled by a potentiostat described by
Harrar and Behrin (21). The counter electrode was grounded.
The voltage output from the load resistor in the feedback loop
was the voltage input (e_{in}) connected to the operational
amplifier integrator shown in figure 3. The output potential
(e_{out}) was the value proportional to the number of coulombs
produced.

Controlled-Potential Coulometry Procedure

Six milliliters of buffer solution was pipetted into
the electrolysis cell over a fresh layer of mercury and the
solution was deoxygenated with nitrogen gas for fifteen minutes

FIGURE 3
OPERATIONAL AMPLIFIER INTEGRATOR

before adding weighed samples. During the deoxygenation process the mercury was stirred. After the fifteen minute deoxygenation, milligram amounts of sample were added to the cell solution. Again nitrogen gas was bubbled through the solution and mercury layer stirring was continued to speed up the electrolysis reaction. Both nitrogen bubbling and stirring were continued throughout the coulometry experiment.

Connections were made from the potentiostat to the saturated calomel electrode, counter electrode, and working electrode. Then the proper working electrode potential versus the saturated calomel electrode was applied. All working electrode potentials were selected after polarography. This reduction potential occurred at a potential on the sample wave plateau but before the potential where other components started to reduce.

The coulometry experiments were conducted for one hour and one-half hour periods. One hour under the above conditions was enough time for essentially complete reduction in pH 4.9 buffer and one-half hour in pH 11.8 buffer of all compounds studied. This was enough time for reduction because after these times there was negligible increase in output voltage. The output voltage (e_{out}) was related directly to the number of coulombs of the electrolysis. This relationship is shown below as a consequence of the electronic set-up for coulometric measurements in figure 3.

The mathematical computation is as follows:

(1) $q = \int_0^t i \, dt$ where q = number of coulombs produced.

i = current.

t = time.

$e_{out} = \dfrac{-1}{RC} \int_0^t e_{in} \, dt$ where e_{in} = potential input to integrator.

$e_{out} = \dfrac{-1}{RC} \int_0^t i R_m \, dt$ by Coulombs Law e = iR

$e_{out} = \dfrac{-R_m}{RC} \int_0^t i \, dt$ by rearrangement.

$e_{out} = \dfrac{-R_m q}{RC}$ by substitution from (1).

Since the measured voltage was attenuated, the terms of the actual equation used was

$q = -e_{out} \dfrac{RC}{R_m} \times \dfrac{1}{X}$ X = attenuator factor

Also, $q = nFN^o$ and $n = \dfrac{q}{N^o F}$ where n = number of electrons involved in electrolysis, q = number of coulombs produced, N^o = number of moles of compound analyzed, F = 96,500 or one Faraday of electricity. Since q was calculated previously, F is a constant and N^o is known from the molecular weight and weight of the compound being analyzed, n can be calculated.

After complete reduction of the coulometric solution, the solutions were transferred to a 50-ml beaker. Two milliliters of 1N hydrochloric acid solution was added to the pH 11.8 buffer solution. The solutions were evaporated over a steam bath. During the evaporation, a stream of nitrogen gas was kept over the solution. The coulometric residue was ready for silylation (which is described in the following silylation procedure).

Procedure for Silylation of Standard Compounds and Products Obtained after Controlled-Potential Coulometry

Two milligrams of each standard were weighed to the nearest one-tenth of a milligram. The weighed standards consisted of the following organic compounds:

1. p-aminophenol
2. p-nitrosophenol
3. p-nitrophenol
4. 1-amino-2-naphthol hydrochloride
5. 4-amino-1-naphthol hydrochloride
6. Orange I
7. Orange II
8. p-(p-hydroxyphenylazo)benzenesulfonic acid sodium salt
9. hydroquinone

Each weighed compound was transferred into a separate glass vial. Two milliliters of N,O-bis-(trimethylsilyl)acetamide (BSA) was pipetted into each sample vial and the vials were stoppered overnight for complete formation of silyl derivatives

at normal laboratory conditions. Orange I and Orange II did
not dissolve in the BSA, indicating the silyl reactions may
not occur.

The coulometry reaction product residues after evap-
oration were treated in the same manner as the standard com-
pounds. Two milliliters of BSA were pipetted into the beaker
containing the residue. The beaker was covered with parafilm
for overnight reaction for complete formation of any silyl
derivatives. At this stage the BSA which contains the silyl
derivatives was now ready for injection onto the gas chromato-
graph so that the silyl derivatives could be separated.

Gas Chromatography of BSA Silyl Derivatives

A Hewlett-Packard Model 5750 Gas Chromatograph was used
for this study. Two microliters (μl) of the BSA containing
the silyl derivatives were injected onto the gas chromatograph
with the aid of a 10-μl syringe. The syringe filling technique
was important so that the entire two microliters of BSA could
be analyzed on the gas chromatograph. This technique requires
neat BSA to be first drawn into the syringe followed by a
small air gap and finally the two microliters of sample was
drawn.

This total volume was injected onto a six foot long
glass column of 2 mm inside diameter. The column was packed
with 3% OV-17 (50:50 methyl phenyl silicone gum) on
Chromosorb W-HP, 80/100 mesh. The column conditions were the
same as those listed in table 1. The detection of the silyl

TABLE 1

GAS CHROMATOGRAPHIC CONDITIONS

Inlet Temperature   = 200° C with column at $\sim$ 25° C

Column Temperature   = 95° C for silyl derivatives of
p-nitrosophenol and hydroquinone

Column Temperature   = 110° C for silyl derivatives of
p-aminophenol, p-nitrosophenol,
p-nitrophenol

Column Temperature   = 145° C for silyl derivatives of
1-amino-2-naphthol hydrochloride
and 4-amino-1-naphthol hydrochloride

Detector Temperature   = 280° C with column at $\sim$ 25° C

Column Helium Flow   = 60 ml/minute

Flame Hydrogen Flow   = 45 ml/minute

Flame Air Flow   = 400 ml/minute

Helium Make-Up Flow   = 90 ml/minute

Recorder Chart Speed   = 0.25 inch/60 seconds

derivatives was by flame ionization.

Polarography and Coulometry

The polarography and coulometry systems were tested for performance using the reduction of cadmium chloride in aqueous solution. The reduction of cadmium chloride has been studied extensively by polarography and coulometry. Thus, by knowing the fact that cadmium (II) is reduced by electrolysis to cadmium amalgam, the polarography experiment was performed on cadmium chloride and a polarogram was obtained which gave a wave due to the known reduction. The working electrode potential was selected from the polarogram to be used for the coulometry experiment. The coulometry was performed and after final calculation the n value was 1.9, which is very close to the expected value of 2. Establishment of good results on cadmium (II) reduction after polarography and coulometry, concluded that these instrumentation systems were acceptable for further use.

Ethanol was used in buffer preparation to aid in dissolving the organic compounds. Nitrogen gas bubbling was necessary for both polarography and coulometry solutions since dissolved oxygen is active during electrolysis reduction. Nitrogen bubbling for fifteen minutes was needed to exclude dissolved oxygen from the solution. The addition of TRITON X-100 to polarography solutions was needed in order to suppress maxima or humps in the plateau region. These humps are caused by a potential dependent absorption phenomenon on the dropping mercury electrode.

RESULTS AND DISCUSSION OF THE EXPERIMENTS

Polarography and Coulometry

The polarography and coulometry systems were tested for performance using the reduction of cadmium chloride in aqueous solution. The reduction of cadmium chloride has been studied extensively by polarography and coulometry. Thus, by knowing the fact that cadmium (II) is reduced by electrolysis to cadmium amalgam, the polarography experiment was performed on cadmium chloride and a polarogram was obtained which gave a wave due to the known reduction. The working electrode potential was selected from the polarogram to be used for the coulometry experiment. The coulometry was performed and after final calculation the n value was 1.9, which is very close to the expected value of 2. Establishment of good results on cadmium (II) reduction after polarography and coulometry, concluded that these instrumentation systems were acceptable for further use.

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Polarograms (current in microamperes versus applied potential in volts) gave the usual wave patterns expected from the dropping mercury electrode. As expected, current oscillated during the potential scan because at any applied potential the current increases as the mercury drop grows in size and the current drops off sharply as the drop detaches itself from the capillary tube. Polarograms illustrated in this paper were constructed by a smooth curve which represents the midpoints of the current maxima and minima. Individual experimental polarograms of the electrolysis reduction of p-nitrosophenol, p-nitrophenol, p-(p-hydroxyphenylazo)benzene-sulfonic acid sodium salt, Orange I, and Orange II in both acidic and basic buffer solutions are shown in figures 4 to 8. The final current rise which is seen in all the polarograms was due to the reduction of other components used in the buffer preparation.

Half-wave potentials were found from the polarograms of electrolysis reduction reactions of the different compounds by measuring the midpoint of the resultant current of the start of the wave and the wave plateau. A line parallel to the wave plateau and through the midpoint was drawn. From the point where this parallel line intersected the wave, a vertical line was dropped to the potential axis and this potential value was the uncorrected half-wave potential. Half-wave potentials for this work are listed in table 2.

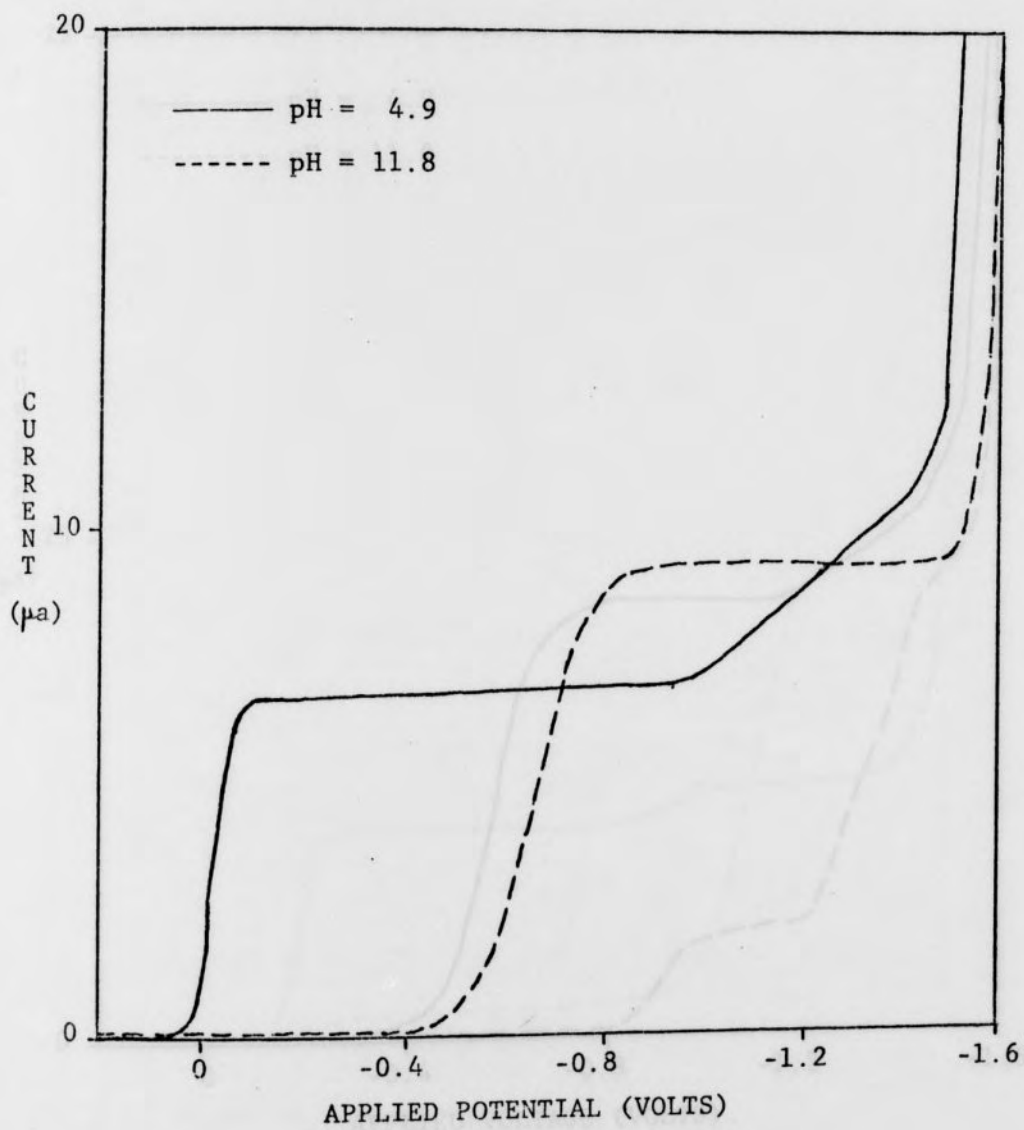# FIGURE 4

POLAROGRAM OF P-NITROSOPHENOL

FIGURE 4 — POLAROGRAM OF P-NITROSOPHENOL

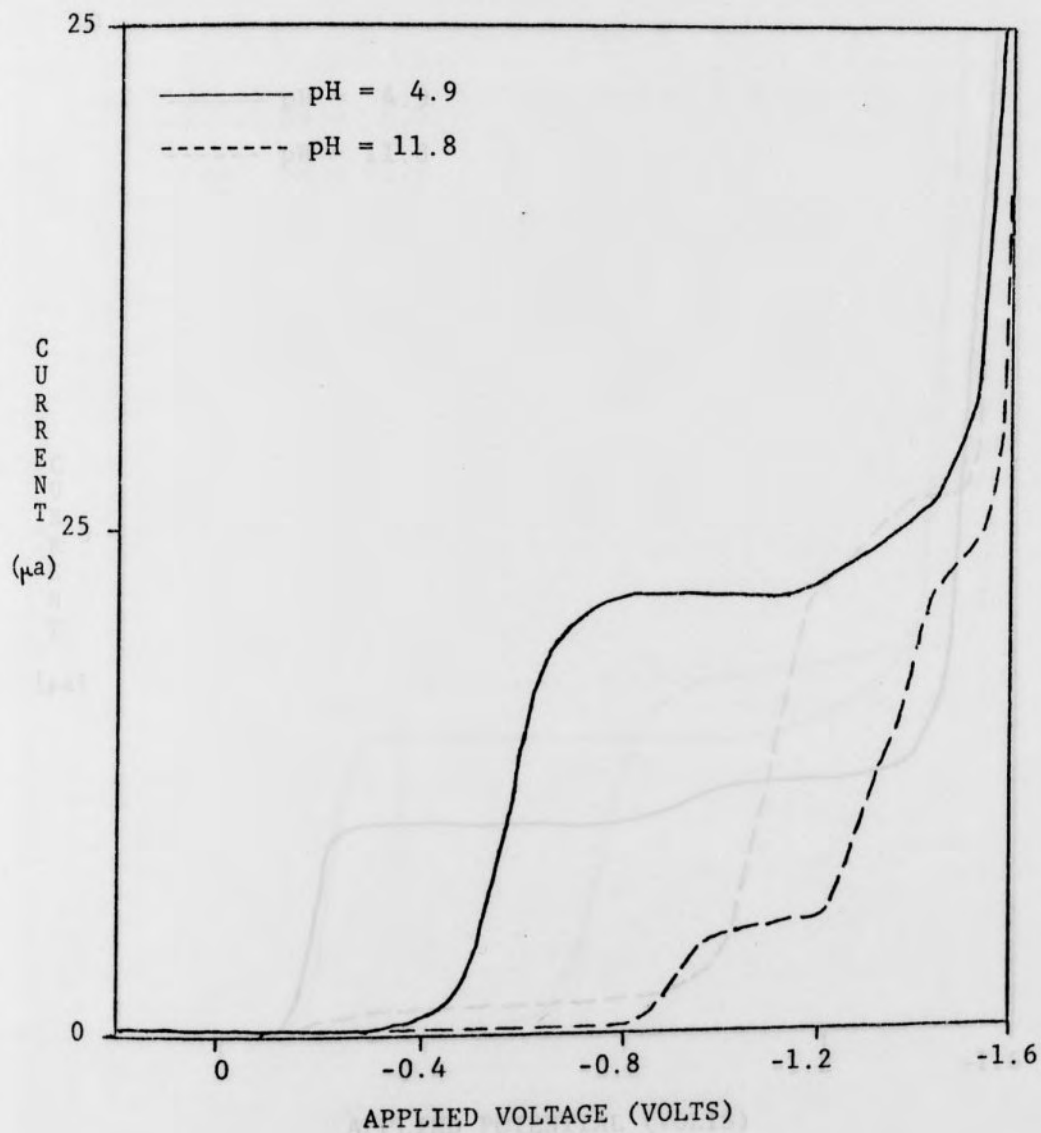# FIGURE 5

POLAROGRAM OF P-NITROPHENOL

FIGURE 6

POLAROGRAM OF P-(P-HYDROXYPHENYLAZO)-
BENZENE SULFONIC ACID SODIUM SALT
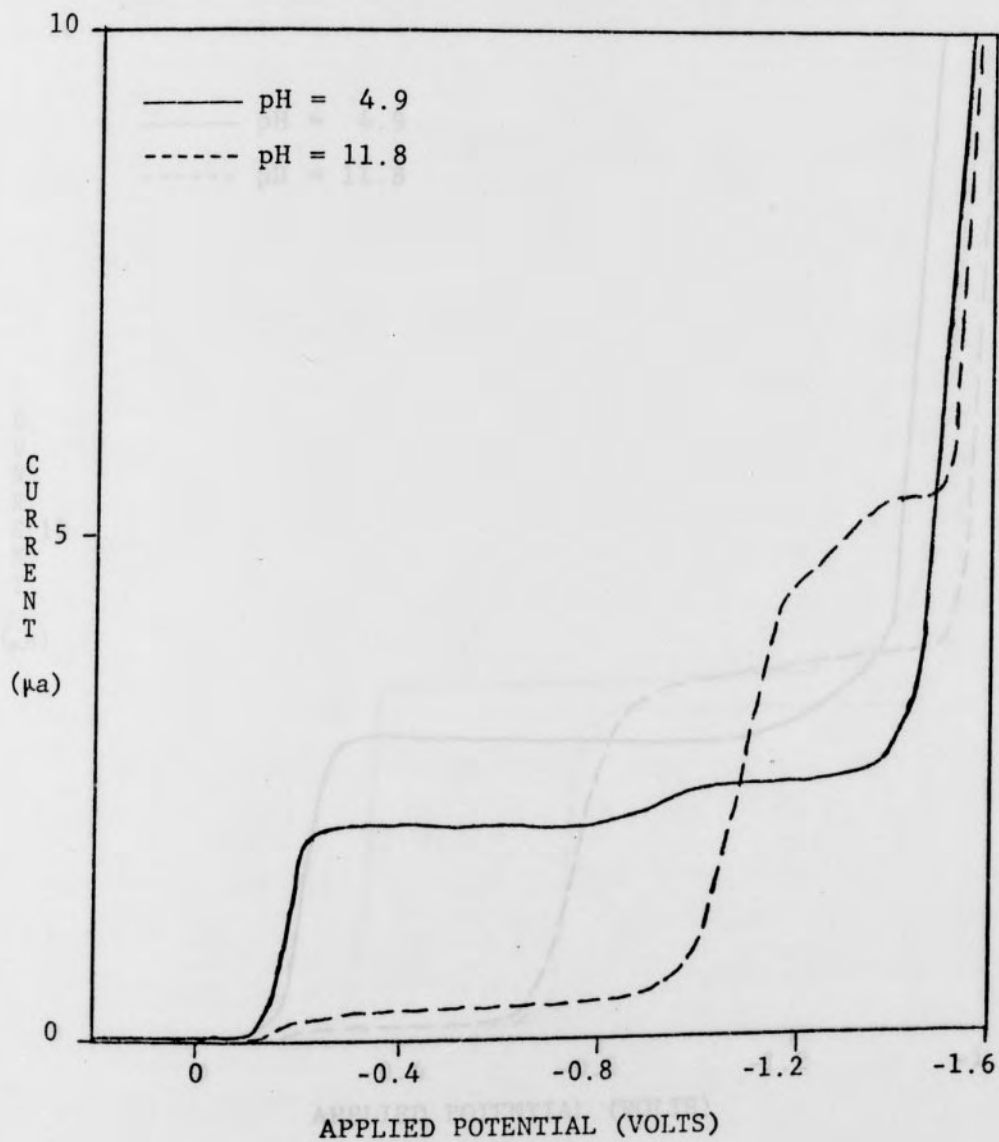
FIGURE 7

POLAROGRAM OF ORANGE I
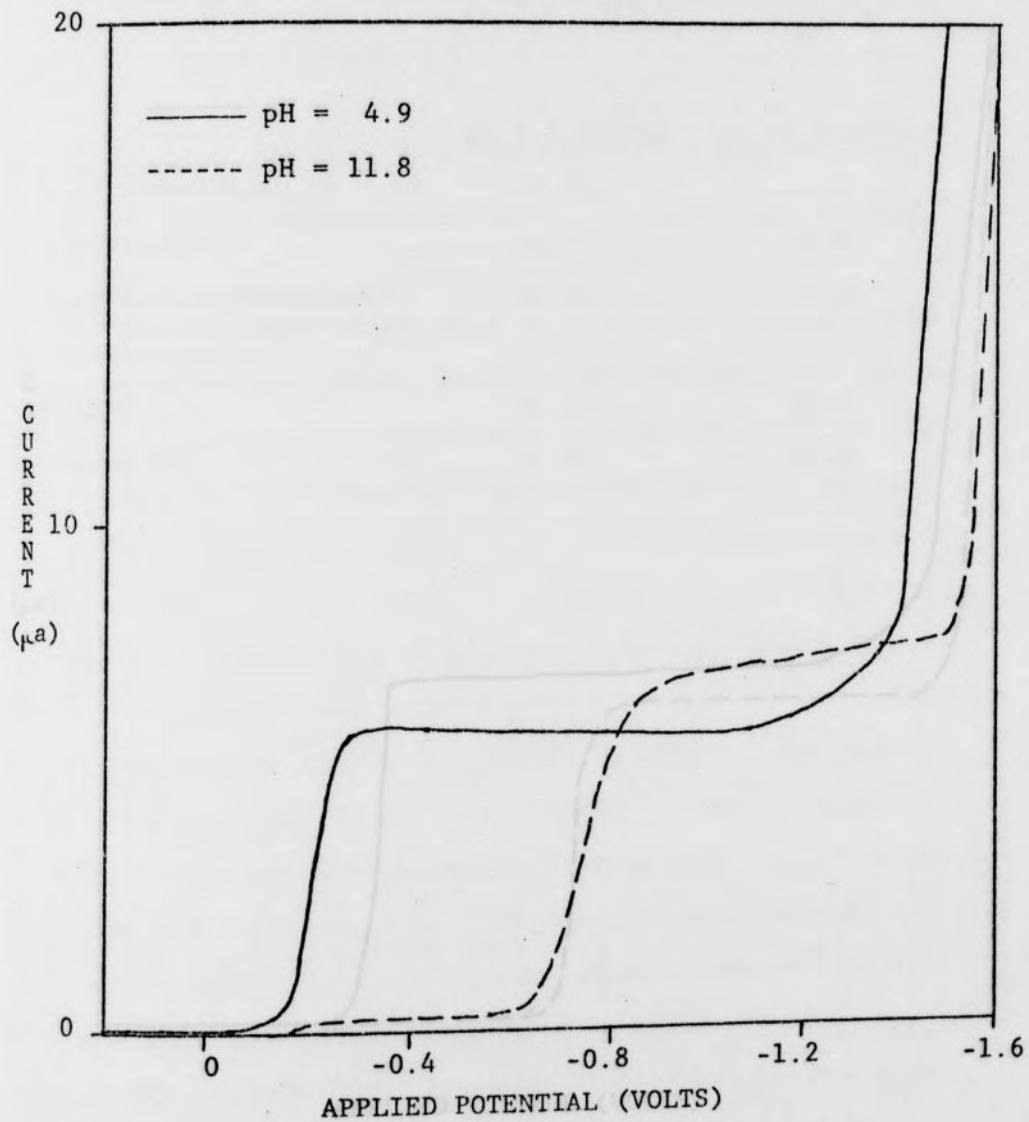
FIGURE 8

POLAROGRAM OF ORANGE II
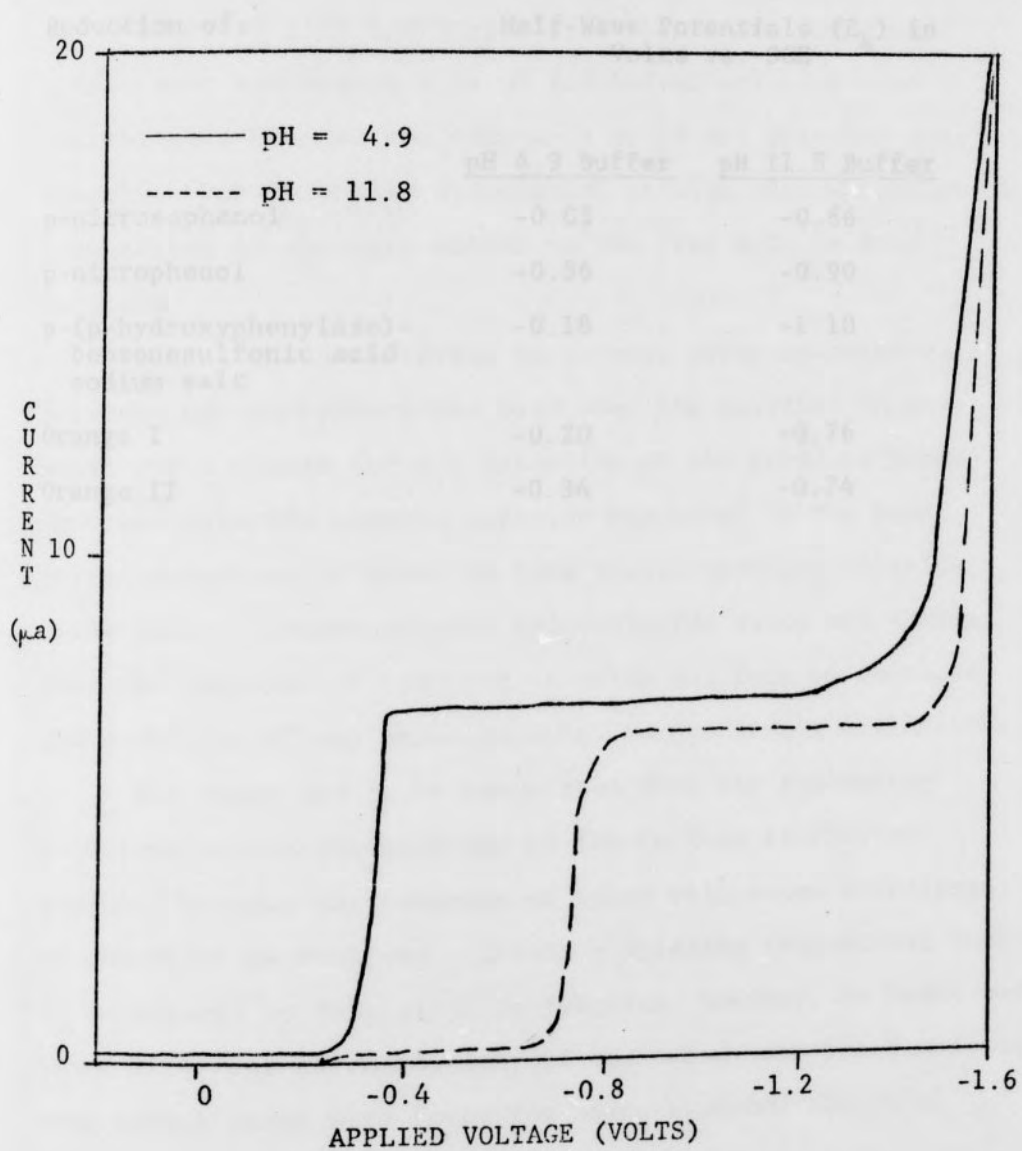
TABLE 2
HALF-WAVE POTENTIALS

Reduction of:	Half-Wave Potentials ($E_{\frac{1}{2}}$) in Volts vs. SCE	
	pH 4.9 Buffer	pH 11.8 Buffer
p-nitrosophenol	-0.03	-0.66
p-nitrophenol	-0.56	-0.90
p-(p-hydroxyphenylazo)-benzenesulfonic acid sodium salt	-0.18	-1.10
Orange I	-0.20	-0.76
Orange II	-0.34	-0.74

The working electrode potentials in volts (v) for all compounds studied are found in table 3. Values of n obtained after coulometric analysis of all compounds in pH 4.9 and pH 11.8 buffer solutions are shown in Table 4. Calculations of n values of p-(p-hydroxyphenylazo)benzenesulfonic acid sodium salt and Orange I in pH 4.9 buffer solution were unattainable because the compounds would not dissolve completely. Possibly this dissolution problem occurs because of protonation of the salt anions to the free acid in acid solution.

During the evaporation to dryness after coulometry, a nitrogen gas atmosphere was used over the solution in case there was a chance for air oxidation of the products formed. Hydrogen chloride aqueous solution was added to the basic buffer solutions in order to form stable hydrogen chloride amine salts. Amino-naphthol hydrochloride salts are stable, thus the addition of hydrogen chloride was done to increase the stability of any amino-naphthol formed during coulometry.

All water had to be evaporated from the coulometry solutions before the addition of BSA to form silylation products because any presence of water will cause hydrolysis of the silyl derivatives. Trisil silylating reagent was used in an attempt to form silyl derivatives, however, no peaks were found after gas chromatography of the amino-naphthol standards even though peaks were found for amino-naphthol BSA silyl derivatives.

TABLE 3

COULOMETRY WORKING ELECTRODE POTENTIAL
(VOLTS VS. SCE)

Compounds	pH 4.9 Buffer	pH 11.8 Buffer
p-nitrosophenol	-0.60	-1.00
p-nitrophenol	-0.80	-1.40

p-(p-hydroxyphenylazo)-
  benzenesulfonic acid
  sodium salt
	-0.60	-1.40

Orange I	-0.40	-1.20
Orange II	-0.60	-1.20

TABLE 4
N VALUE CALCULATED AFTER COULOMETRY

Compound	pH 4.9 Buffer	pH 11.8 Buffer
p-nitrosophenol	4.2	3.8
p-nitrophenol	6.6	6.0
p-(p-hydroxyphenylazo)- benzenesulfonic acid sodium salt	didn't dissolve completely	3.8
Orange I	didn't dissolve completely	4.1
Orange II	3.5	4.6

Figures 9 through 11 show the gas chromatograms of BSA silyl derivative standards. Figure 9 shows the separation of p-nitrosophenol and hydroquinone at 95° C, figure 10 shows the gas chromatographic separation of p-aminophenol, p-nitrosophenol, and p-nitrophenol, and figure 11 shows the separation of 1-amino-2-naphthol hydrochloride and 4-amino-1-naphthol hydrochloride. No peaks were found from the Orange I and Orange II silylated standards indicating derivatives may not have been formed.

The retention times of standard silylation derivatives in seconds were determined from the chromatograms by using the BSA solvent peak as the starting point of the chromatogram. The distance from the starting point to the peak maximum of the standard silylated peak was measured on each chromatogram. This distance in inches divided by the recorder chart speed represented the retention times in seconds for the standard silylated compounds. Table 5 shows the retention times for the different silyl standard compounds at the relative gas chromatography column temperatures. The hydrochloride salt of p-aminophenol and p-aminophenol standard silyl derivatives gave the same retention times.

Gas chromatography of BSA silyl derivatives of the coulometry residues gave peaks at the retention times that matched the silyl standard compounds listed in table 6.

Standard p-aminophenol, equivalent in weight to that expected after coulometric reduction of p-nitrosophenol, was

FIGURE 9

CHROMATOGRAM AT 95° TEMPERATURE

PEAK #

1. p-nitrosophenol

2. hydroquinone
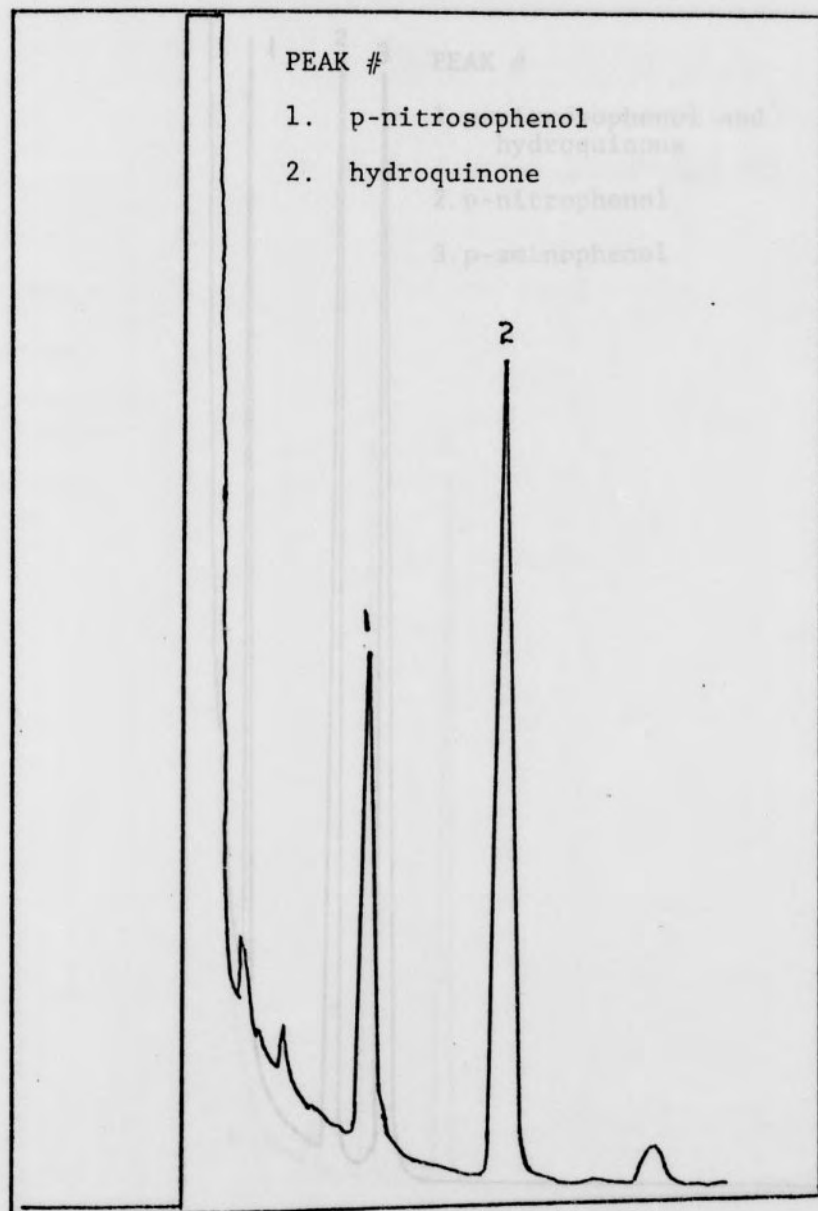
FIGURE 10

CHROMATOGRAM AT 110° TEMPERATURE

PEAK #

1. p-nitrosophenol and hydroquinone

2. p-nitrophenol

3. p-aminophenol
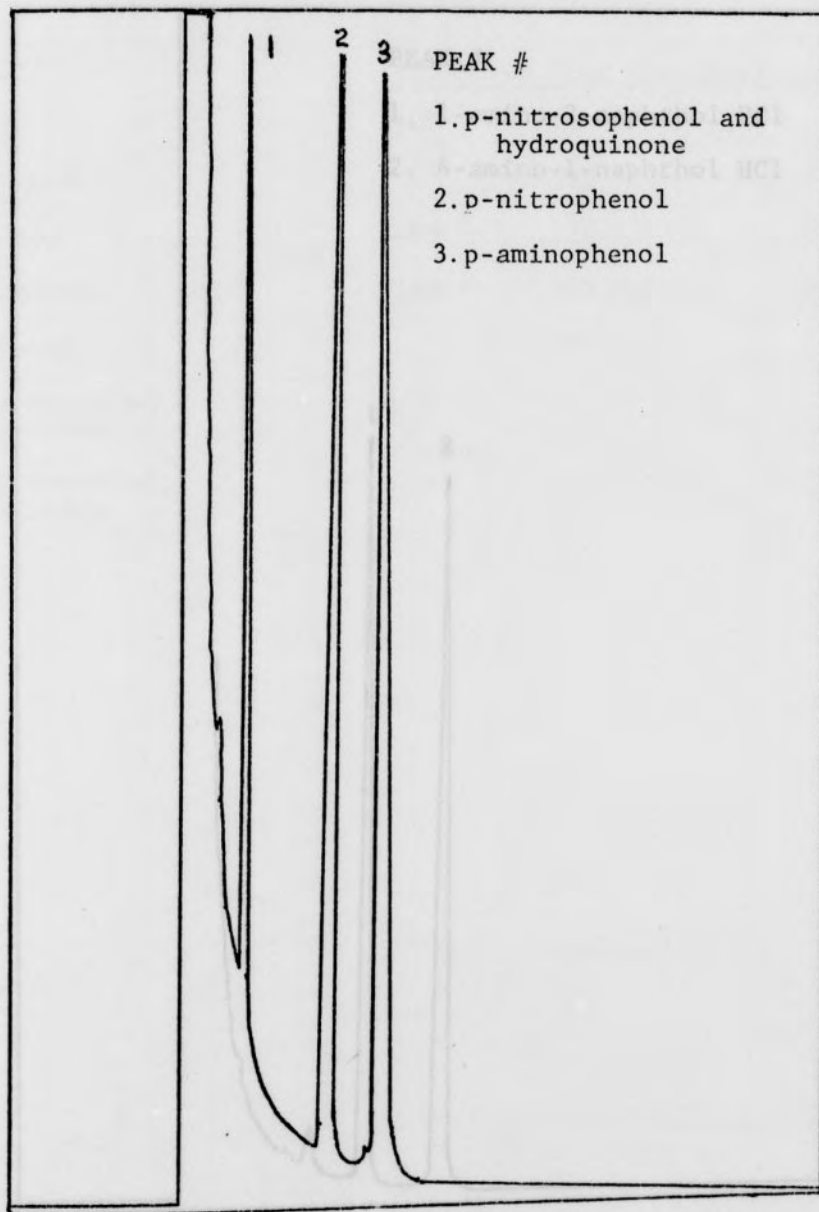
FIGURE 11

CHROMATOGRAM AT 145° TEMPERATURE

PEAK #

1. 1-amino-2-naphthol HCl

2. 4-amino-1-naphthol HCl

TABLE 5

GAS CHROMATOGRAPHIC RETENTION TIMES OF SILYL
DERIVATIVE STANDARDS

Compound	Retention Time (Seconds)		
	95°	110°	145°
p-aminophenol		391	
hydroquinone	480	130	
p-nitrosophenol	269	125	
p-nitrophenol		295	
1-amino-2-naphthol hydrochloride			379
4-amino-1-naphthol hydrochloride			494

TABLE 6

COULOMETRY RESIDUE IDENTIFICATION
BY RETENTION TIME COMPARISON

	Coulometry Product Identified	
Coulometry of:	pH 4.9 Buffer	pH 11.8 Buffer
p-nitrosophenol	p-aminophenol	p-aminophenol
p-nitrophenol	p-aminophenol	p-aminophenol
p-(p-hydroxyphenylazo)- benzenesulfonic acid sodium salt	p-aminophenol	p-aminophenol
Orange I	no peak	no peak
Orange II	no peak	no peak

taken through the entire procedure from introduction into buffer solution to gas chromatography of the silyl derivative to find the percent recovery. It was found 90% of p-aminophenol was recovered when compared to p-aminophenol that was not taken through the procedure. Ninety percent of reduced p-nitrosophenol was recovered as p-aminophenol. The peak heights were used to calculate the percent recovery.

Another procedure was attempted to isolate the aromatic amine phenol compounds expected after coulometry. Sodium bicarbonate was added to the resultant coulometry solution and this aqueous solution was extracted with n-butanol-ethyl ether 1:1 by volume. The aromatic amino phenols were extracted into the organic layer. The organic phase was treated with anhydrous sodium sulfate to remove any water. The organic solvent was evaporated to dryness and the residue was treated with BSA. However, low recovery of less than 10% of p-amino-phenol was found.

CONCLUSIONS BASED ON RESULTS

The electrochemical reactions below are determined from consideration of the n value calculations (number of electrons involved in the reaction) and identification of the products after controlled-potential coulometry of starting materials in both pH 4.9 and pH 11.8 buffer solutions.

I. Reduction of p-nitrosophenol where n = 4 and p-aminophenol is obtained as the coulometry product in both pH 4.9 and pH 11.8 buffers.

A.

$$+ 2e^- + 2H^+ \longrightarrow \xrightarrow[2H^+]{2e^-} + H_2O$$

B.

$$+ 4e^- + 4H^+ \longrightarrow + H_2O$$
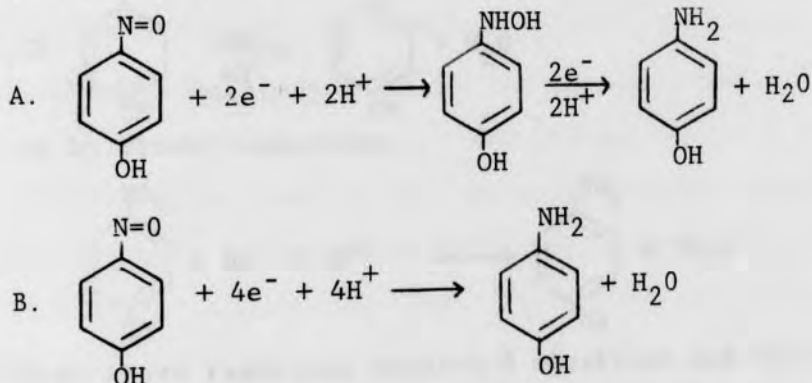
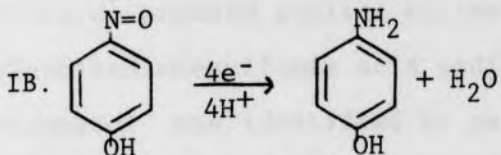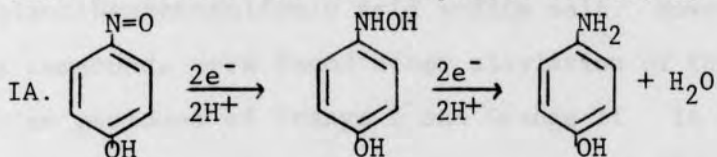Both of the above reactions involve the four electron reduction and give p-aminophenol as the product. As stated in a paper by Alberts & Shain, (10), reaction IA takes place in low pH solution and IB occurs in high pH solution. Their polarography on reduction of p-nitrosophenol in pH 4.9 buffer showed two waves while the polarography in pH 11.8 buffer requires one wave. Our polarography confirms their findings.

II. Reduction of p-nitrophenol where n = 6 and p-amino-
phenol is the coulometry product.

A. $+ 2e^- + 2H^+ \longrightarrow$ $+ H_2O$
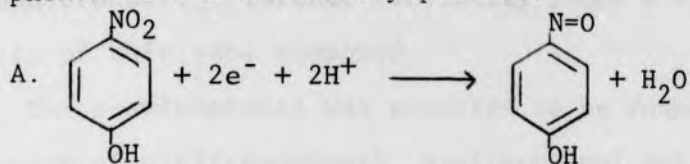
Then as before the nitrosophenol reduces as

IA. $\xrightarrow[2H^+]{2e^-}$ $\xrightarrow[2H^+]{2e^-}$ $+ H_2O$

IB. $\xrightarrow[4H^+]{4e^-}$ $+ H_2O$

or by direct reduction

 $+ 6e^- + 6H^+ \longrightarrow$ $+ 2H_2O$
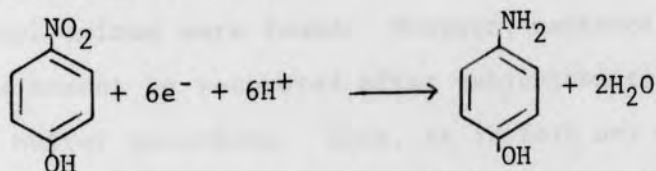
All these above reactions involve 6 electrons and the final
product is p-aminophenol. The p-aminophenol product was pro-
posed in a mechanism by Lindbeck and Freund (14).

III. Reduction of p-(p-hydroxyphenylazo)benzenesulfonic acid
sodium salt where n = 4 and p-aminophenol is the coulometric
product.

A. HO—⟨⟩—N=N—⟨⟩—SO₃Na $\xrightarrow[2H^+]{2e^-}$ HO—⟨⟩—N-N—⟨⟩—SO₃Na

or

$2e^- \Big| 2H^+$

B. HO—⟨⟩—N=N—⟨⟩—SO₃Na $\xrightarrow[4H^+]{4e^-}$ HO—⟨⟩—NH₂ + H₂N—⟨⟩—SO₃Na
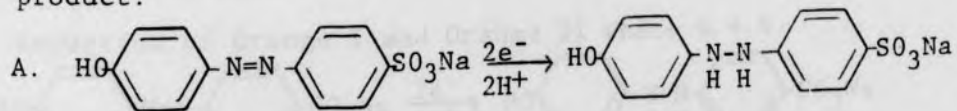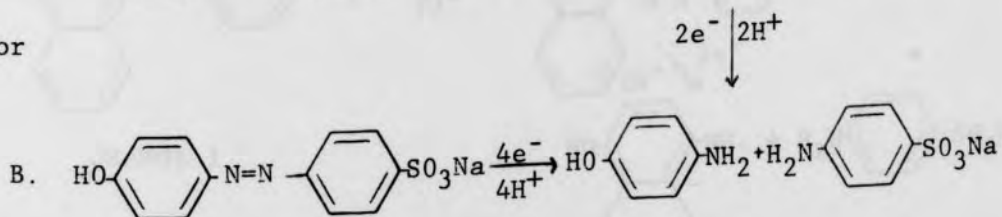
Both IIIA and IIIB involve 4 electrons and p-aminophenol is the end product. Florence (16,17,18) found n = 4 in coulometric studies of this same compound.

The p-aminophenol was expected to be found from the reduction of p-nitrosophenol, p-nitrophenol and p-(p-hydroxy-phenylazo)benzenesulfonic acid sodium salt. However, no naphthol amine compounds were found after silylation of the coulometric reaction residues of Orange I and Orange II. It is felt the re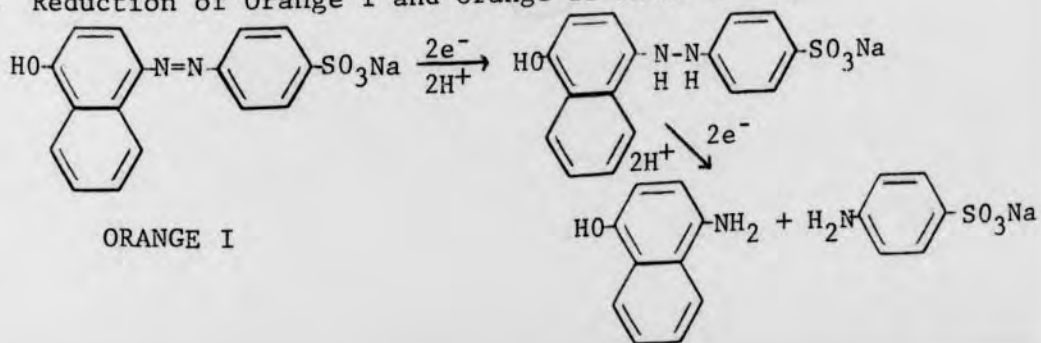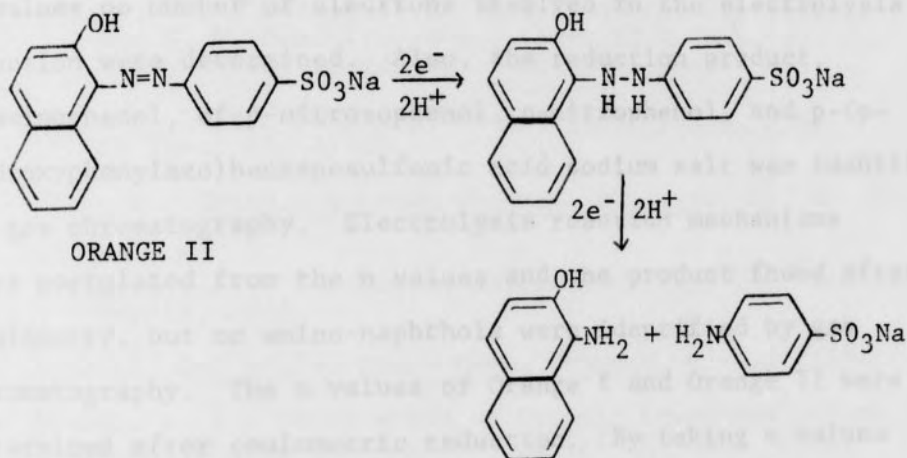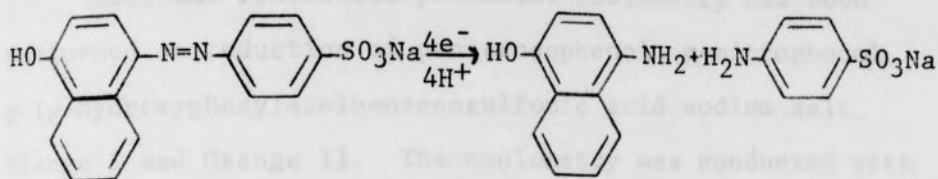actions do proceed similar to the reaction of p-(p-hydroxy-phenylazo)benzenesulfonic acid sodium salt where n = 4 and p-aminophenol was identified by gas chromatography in the coulometric residues. Orange I and Orange II have n = 4 and no naphthol amines were found. However, naphthol amine standards cannot be recovered after subjection to the pH 4.9 and 11.8 buffer solutions. Thus, it is felt any naphthol amines produced from the coulometry of Orange I and Orange II take the same course as the standard naphthol amines and cannot be recovered for identification by gas chromatography. The Orange I and Orange II reduction reactions which were also proposed by Florence (16,17,18) (that we can only assume to occur) are shown below.

IV. Reduction of Orange I and Orange II where n = 4.

ORANGE I

Or by direct reduction

$$HO-\text{(naphthyl)}-N=N-\text{(phenyl)}-SO_3Na \xrightarrow[4H^+]{4e^-} HO-\text{(naphthyl)}-NH_2 + H_2N-\text{(phenyl)}-SO_3Na$$

$$\underset{\text{ORANGE II}}{OH\text{-(naphthyl)}-N=N-\text{(phenyl)}-SO_3Na} \xrightarrow[2H^+]{2e^-} OH\text{-(naphthyl)}-\underset{H\ H}{N-N}-\text{(phenyl)}-SO_3Na$$

$$\xrightarrow[2H^+]{2e^-}$$

$$OH\text{-(naphthyl)}-NH_2 + H_2N-\text{(phenyl)}-SO_3Na$$

Or by direct reduction

$$OH\text{-(naphthyl)}-N=N-\text{(phenyl)}-SO_3Na \xrightarrow[4H^+]{4e^-} OH\text{-(naphthyl)}-NH_2 + H_2N-\text{(phenyl)}-SO_3Na$$
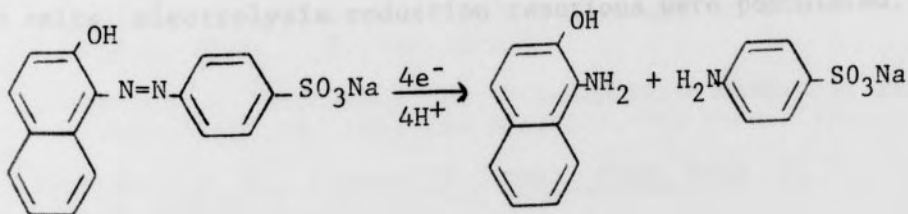
SUMMARY

Constant controlled-potential coulometry has been performed on reduction of p-nitrosophenol, p-nitrophenol, p-(p-hydroxyphenylazo)benzenesulfonic acid sodium salt, Orange I and Orange II. The coulometry was conducted with the above compounds in acid and base buffer solution of pH 4.9 and pH 11.8 respectively. In performing the coulometry, n values or number of electrons involved in the electrolysis reaction were determined. Also, the reduction product, p-aminophenol, of p-nitrosophenol, p-nitrophenol, and p-(p-hydroxyphenylazo)benzenesulfonic acid sodium salt was identified by gas chromatography. Electrolysis reaction mechanisms were postulated from the n values and the product found after coulometry, but no amino-naphthols were identified by gas chromatography. The n values of Orange I and Orange II were determined after coulometric reduction. By taking n values and the similarities of Orange I and Orange II to p-(p-hydroxyphenylazo)benzenesulfonic acid sodium salt as all being azo salts, electrolysis reduction reactions were postulated.

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