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Electrolytic reduction of some N-nitro compounds.

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Thesis
Electrolytic Reduction of Some N-Nitro Compounds

by
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Introduction

Many organic compounds have been reduced electrolytically, in many cases in good yields. The method is also, in those cases where it has been used, a gentle method, less likely to cause changes in the molecule or rupture of the molecule than other methods of affecting reductions. As an example, ketones which are sensitive to acids or bases thus precluding the Clemmenson or Wolff-Kishner methods of reduction can be reduced by the electrolytic method without causing rupture of the molecule.

The electrolytic method is amenable to a choice of conditions such as temperature, electrolyte, pH, electrode materials; and by varying these factors the proper conditions for the reduction of each molecule to any one of several reduction stages may be found. A nitro compound can be reduced to the nitroso, hydroxylamine, or amine stage by use of the proper electrodes and catholyte.

This is largely an empirical trial and error method but by the use of the polarographic method and microelectrodes of various metals some of the chance can be eliminated, and the method is no longer trial and error but some discretion can be used as to which metals to use in the various solutions to approximate the voltage necessary for the desired reduction.

Both the electrolytic method and the polarographic method were used.
Part I. Preparation of Nitrocarbamates and Nitroamines

The ethyl N-methylcarbamate was prepared by adding ethyl chloroformate dropwise to an aqueous solution of methylamine and sodium hydroxide.\(^2\) It was found that the optimum yields, about 87%, were obtained when the temperature of the reaction flask was maintained below 15°C by means of an acetone-dry ice bath. The reaction can be written as

\[
\text{CH}_3\text{NH}_2 + \text{ClCOOC}_2\text{H}_5 + \text{NaOH} \rightarrow \text{CH}_3\text{N}^+\text{COOC}_2\text{H}_5^- + \text{NaCl} + \text{H}_2\text{O}
\]

The ethyl N-methylcarbamate was nitrated using the procedure developed by Mason and Curry.\(^3\) The nitrating agent was fuming nitric acid and acetic anhydride, enough acetic anhydride being used to react with all of the water in the fuming nitric acid and the water released in the reaction. Presumably there is formed a nitronium cation which can attack the negative center of the carbamate.\(^4\)

\[
\text{CH}_3\text{C}^\circ\text{O}^-\text{O}^-\text{CH}_3 + \text{HNO}_3 \rightarrow \text{CH}_3\text{C}^\circ\text{O}^\cdot\text{NO}_2 + \text{CH}_3\text{COOH}
\]

To the solution of acetic anhydride and fuming nitric acid was added the ethyl N-methylcarbamate and the temperature kept between 200°-300°C.

The ethyl N-methyl N-nitrocarbamate was distilled under reduced pressure since it decomposes at temperatures of about 100°C. It was found that a water pump does not lower the pressure sufficiently to distill the nitrocarbamate without decomposition. Even with an oil pump, the temperature for spontaneous decomposition was reached in the distilling flask when too long a fractionating column was used. When decomposition
began there was a spontaneous evolution of heat; and with the heating source removed, and at atmospheric pressure, spontaneous distillation of a few milliliters of material occurred at 156°C. Then the temperature of distillation began to drop but spontaneous distillation continued until a temperature of 90°C was reached. Gases were evolved throughout this occurrence.

An attempt to fractionate the decomposition products was unsuccessful; no noticeable break (in the even rise) of temperature occurred.

The reaction can be written as

\[
\text{CH}_3\text{N}^-\text{OOC}_2\text{H}_5 + \text{NO}_2^+ \rightarrow \text{CH}_3\text{N}^+\text{OOC}_2\text{H}_5\text{NO}_2^-
\]

\[
\text{CH}_3\text{N}^-\text{OOC}_2\text{H}_5 + \text{H}^+
\]

The isopropyl ammonium salt of the N-methyl nitroamine was made by adding two moles of isopropylamine to one mole of the ethyl N-methyl N-nitrocarbamate dissolved in ether. The salt was obtained in 99% yield.

\[
\text{CH}_3\text{NOCOC}_2\text{H}_5 + 2 \text{CH}_3\text{C} = \text{NH}_2 \rightarrow \text{CH}_3\text{N}^-\text{OOC}_2\text{H}_5\text{H}_3\text{N}^+\]

The salt was decomposed by dissolving in water and adding hydrochloric acid. Extraction with ether gave only an 18% yield of the methyl nitroamine but continuous ether extraction carried on for three days gave a recovery of another 30% of the product.
Several attempts were made to form the salts of the ethyl N-methyl nitrocarbamate by passing gaseous ammonia, methylamine, and ethylamine through an ether solution of the nitrocarbamate but none of the salt precipitated from the ether solution. A sample from one of these attempts in which ethylamine was passed through an ether solution of ethyl N-methylcarbamate was dried in a vacuum desiccator and allowed to stand at 0°C for five weeks without any precipitate appearing. Various solvents other than ether, such as ligroin, petroleum ether, benzene, toluene, hexane, were also tried but no precipitate appeared.

Experimental:

1. Preparation of Ethyl N-methylcarbamate:

Three hundred sixty-eight gms. (9.2 moles) of sodium hydroxide was dissolved in 510 ml. of water and placed in a three-necked flask equipped with a dropping funnel, mercury seal stirrer, and a thermometer. To the same flask was added 250 gms. (8.05 moles) of methylamine (one kilo 25% \( \text{CH}_3\text{NH}_2 \)) and the flask was cooled with an acetone-dry ice bath. When the temperature fell below 15°C, 855 gms. (7.9 moles) of ethylchloroformate was added dropwise with stirring. The temperature was kept at all times below 15°C.

The reaction mixture consisted of two layers which were separated in a separatory funnel. The bottom layer was extracted with four 300 ml. portions of ether and the ether extracts combined with the top layer.

The top layer and ether extracts were dried with anhydrous potassium carbonate and the ether distilled off on a steam bath. The remainder was vacuum distilled using a fractionating column and 700 gms. (6.8 moles) of
the ethyl N-methylcarbamate was collected between 87°C-87.1°C, pressure 34 mm., representing a yield of 86.2%.

2. Preparation of Ethyl N-methyl-N-nitrocarbamate:

Eight hundred seventy gms. (8.52 moles) of acetic anhydride was placed in a three-necked flask equipped with a dropping funnel, mercury seal stirrer and thermometer. To this was added 642.6 gms. (10.2 moles) of fuming nitric acid dropwise with stirring and cooling of the reaction mixture with an acetone-dry ice bath. The rate of addition was such that the temperature of the reaction mixture did not exceed 10°C.

Then 700 gms. (6.8 moles) of ethyl N-methylcarbamate was added dropwise to the acetic anhydride-fuming nitric acid mixture at such a rate that the temperature remained between 20°C-30°C. Cooling was accomplished by use of an acetone-dry ice bath.

After completion of the addition, the contents of the reaction flask were allowed to cool to a temperature of 0°C, and then were poured into six and one-half liters of water (approximately three times the volume of the reaction mixture) which had also been cooled to 0°C. The nitrocarbamate separated as an oil and was drawn off with a separatory funnel. The water layer was extracted with ether and the ether extracts added to the bottom layer.

The oil and ether extracts were washed repeatedly with 10% K2CO3 until free from acid and then dried by filtering twice through two thicknesses of filter paper. The ether was removed on a steam bath and the oil distilled under vacuum; the product was collected at 70°C, 2 mm. pressure. The yield was 689 gms. (4.65 moles) or 68.5%.
3. Preparation of Isopropylamine Salt of N-Methylnitroamine:

One hundred gms. (0.675 mole) of ethyl N-methyl-N-nitrocarbamate was dissolved in 200 cc. of ether and cooled in an ice-salt bath. To this solution 80 gms. (1.35 moles) of isopropylamine was added over a period of 15 minutes. The solution was vigorously stirred during the addition. The ethereal mixture was cooled an additional half hour and the white solid which precipitated was filtered off and washed with two 25 cc. portions of ether. After drying in a desiccator the solid weighed 90.2 gms. (0.67 mole) and represented a yield of 99%.

The ether solution of the ethyl N-isopropylcarbamate was dried with anhydrous potassium carbonate, the ether and isopropylamine taken off on a steam bath and the residue fractionated under vacuum. One hundred three and eight-tenths gms. of the ethyl N-isopropylcarbamate was collected at 88°C at 35 mm. or a yield of 78.5%.

4. Attempts to Prepare Ammonium Salt of N-Methyl-N-nitroamine:

The ammonia was generated by adding dropwise to a saturated solution of ammonium chloride a 30% sodium hydroxide solution and was dried by passing through two U-tubes containing drierite, then bubbled through 9 gms. (0.061 mole) of ethyl N-methyl-N-nitrocarbamate dissolved in 20 cc. of ether. Only a minute amount of solid precipitate formed when the ammonia was first added and it redissolved. The major portion of the starting compound was recovered when the ether was distilled off.

5. Attempts to Prepare the Methylammonium Salt of N-Methyl-N-nitroamine:

Ten grams (0.0675 mole) of ethyl N-methyl-N-nitrocarbamate was dissolved in 10 cc. of ether. Methylamine was generated by adding dropwise 25%
methylamine to a flask containing solid potassium hydroxide. The amine was dried by passing through a U-tube containing glass beads and a straight tube filled with soda lime and then bubbled into the nitrocarbamate solution in ether until a strong smell of amine could be detected. No precipitate appeared. On evaporation of the ether and vacuum distillation of the residue, all of the ethyl N-methyl-N-nitrocarbamate was recovered.

6. Attempts to Prepare the Ethylammonium Salt of N-Methyl-N-nitroamine:

The amine was prepared and dried in the same way as the methylamine and passed into an ether solution of the ethyl N-methyl-N-nitrocarbamate until a strong amine odor could be detected. No precipitate appeared and on evaporation of the solvent and vacuum distillation, the nitrocarbamate was recovered.

Part II. Attempted Electroreduction of Nitrocarbamates and Nitroamines

Electroreduction and electrooxidation of organic substances are due to the fact that many organic compounds act as depolarizers. Cathodic depolarizers take up hydrogen or yield oxygen or do both simultaneously. Therefore, a cathodic depolarizer is reduced at the cathode during electrolysis. Anodic depolarizers are oxidizable substances.

Electrolysis is the giving off and taking on of electrons. An external source of electrical energy is used to effect chemical reactions. A definite potential is needed to overcome the resistance of the cell and is equal to the IR product, but additional potential is needed to overcome overvoltage.
Overvoltage, or polarization, can be defined as any change produced at an electrode, whatever the means, which causes the single oxidation potential to differ from the theoretical, reversible, value in the particular solution.

The overvoltage usually is small for deposition or solution at metal electrodes; but the overvoltages required for the liberation of gaseous hydrogen or oxygen are high especially on certain metals, the value of this overvoltage being dependent on the electrode material and the solution.

A depolarizer is any substance which reduces polarization and the mechanism may be considered to consist of two parts in cathode depolarization; first, formation of atomic hydrogen at the cathode:

\[ \text{H}^+ + \text{e} \rightarrow \text{H} \]

and second, the reaction of the atomic hydrogen, before its release, with the depolarizer. In this manner the cathode potential may be maintained below that required for hydrogen evolution, and the depolarizer is reduced.

A substance that is reduced at a potential above that required for the liberation of hydrogen is of little use as a cathodic depolarizer and the right electrode materials should be found, which has an overvoltage high enough so that the potential at which hydrogen is liberated is above the potential at which the depolarizer is reduced. Care must be exercised in cases where more than one reductive process can occur that if that reduction is required which needs the smaller potential of two different potentials, the electrode be used which gives a potential for the wanted reduction.

The process of reduction depends not only on the energy of reduction as measured by the cathode potential, but also on the velocity of the
secondary process, or reaction of active hydrogen with the depolarizer.

\[ H^+ + e^- = H \quad (I) \]

\[ H + \text{depolarizer} = \text{reduction} \quad (II) \]

If reaction (I) is faster than reaction (II), concentration of active hydrogen will increase and with it the cathode potential, for

\[ \Pi = RT \ln \frac{C_{H^+}k}{C_H} = \text{cathode potential} \]

and gaseous hydrogen will be given off. To offset the evolution of hydrogen, as large a cathode surface as possible must be used, together with lower current density, and stirring.

The electroreduction of methyl N-nitrocarbamate, ethyl N-nitrocarbamate and nitrourea have been reported by H. J. Backer who also reported the reduction of N,N-dimethyl-N-nitroamine electrically using a tinned copper cathode and 10% sulfuric acid, sodium acetate solution, or acetic acid solution as the catholyte; the anolyte used was 20% sulfuric acid and the anode was of lead.

The procedures of the above worker were essentially repeated with ethyl N-methyl-N-nitrocarbamate and N-methyl-N-nitroamine.

In the case of ethyl N-methyl-N-nitrocarbamate, evidence of reduction was found, but in the case of the N-methyl-N-nitroamine no such evidence could be found. No derivatives of the hydrazines could be prepared and in every case where the reducing material was isolated, it was found to be inorganic and most probably the reduced form of the metal which was used as the cathode. The basis for the percentages of hydrazine formed from the N-nitroamines given in the experimental portion of this thesis was the Siggia method of titration. The reagent used in this method was
iodine which under the conditions used could react with any reduced form of a metal, as stannous ion, to give iodide ion. In all cases, with one exception, where isolation of hydrazine was attempted, none could be found even though iodine was used up. In view of these two facts it seems justifiable to assume that no reduction of the nitroamines to hydrazines occurred. The exception which justifies the assumption that a hydrazine was formed is the reduction of experiment II.

Three different metals were used for electrode material in our experiments in various catholytes in the hope that the right conditions of potential for reduction of the nitroamine to the hydrazine might be found. It was the pure chance involved in pursuing this line of inquiry further that led us to investigation of the polarographic method as a probe for finding the right conditions. This aspect of the problem will be dealt with more fully in Part III of this report.

The circuit which was used was designed by us and included a standard half cell by means of which the voltage of the cathode could be measured using a student potentiometer which is shown above the dotted line in the circuit drawing. A calomel half cell, ST., was used to measure the electromotive force of the tinned copper cathode, and the circuit was completed by means of an agar salt bridge (B)¹⁰ one end of which dipped into a beaker containing normal potassium chloride and the other end of which dipped into a modified Luggin capillary (L).¹¹ The voltage drop across the reduction cell was measured by a voltmeter V. The current through the reduction cell and coulometer B was measured by the ammeter I and controlled by a resistance R.
The coulometer was used to accurately determine the amount of current (which passed through the cell). A copper coulometer was chosen and the amount of current could be calculated as follows: Since 26.8 ampere hours are needed to deposit an equivalent weight of copper:

\[
\frac{\text{wgt. copper}}{\text{Equiv. wgt. copper}} = \frac{\text{no. of ampere hours}}{26.8 \text{ ampere hours}}
\]

The theoretical amount of current needed is dependent on the amount of material and the change in oxidation number. Since the nitro group is 

\[ (+3) \rightarrow (-3) \]

reduced to the amine group, \(-\text{NO}_2 \rightarrow -\text{NH}_2\), six faradays are needed
per mole or

\[
\frac{\text{Wgt. used}}{\text{Mol. wgt.}} = \frac{\text{Amt. current (in Faradays)}}{6}
\]

\[
\text{Amt. current (in Faradays)} \times 26.8 = \text{Number ampere hours needed.}
\]

The length of time for the reduction, which is a function of the current, is found by first determining the current density, which is the number of amperes flowing into a unit electrode surface. This value times the area of the cathode is the strength of the current which divided into the amount of current (ampere-hours) needed gives the length of time that current should be on at any given current strength.

The modified Luggin capillary\(^3\) was used to measure the electromotive force of the cathode. This is an open tube drawn out at its lower end in a bent capillary about one mm. in diameter and fixed into position pressed lightly on the cathode. Into this tube is introduced one end of the salt bridge. The circuit may be completed by means of the key (K).

The electroreductions were carried out in a beaker placed in a larger beaker in which ice could be put for cooling. In the middle beaker was placed the cylindrical lead anode inside of which was placed the diaphragm, a porous cup, which thus separated the beaker into inner and outer compartments. This prevented the material which was reduced at the cathode from being oxidized at the anode. A rubber stopper was used on the porous cup through which extended the Luggin capillary, a reflux condenser, a stirrer and the leads of the cathode.
As cathode, copper mesh \(^6\) which had been tinned was used in most experiments but an anodized nickel cathode and anodized Pb cathodes were also tried. The electrodes were built by us to fit the equipment; the leads were all fused into glass tubing for two reasons: first to keep the area of the electrode in contact with the electrolyte constant, and second that there be no corrosion due to fumes of the electrolytes and that no corrosion products fall into the electrolyte to contaminate it.

The solution used to plate the copper mesh electrodes consisted\(^{13}\) of 30 g. of stannous chloride dihydrate, 75 g. of sodium hydroxide, and 60 g. of glucose per liter of solution. The tinning was carried out at a temperature of 60°C and with a current density of 0.5 to 1 ampere per square decimeter.

The anodization of the cathodes,\(^{14}\) not of the electroplates, was done by placing the cathode in the center of a beaker containing a solution of 20% sulfuric acid, making sure that the acid covered the cathode
completely. An aluminum sheet was placed around the cathode which was then connected to the positive terminal of the source of current, aluminum to the negative terminal. The current was turned on for two minutes at an anode current density of 0.02 ampere per square centimeter. The current was turned off, the bath removed and the cathode washed thoroughly with distilled water.

Lead cathodes were anodized\textsuperscript{15} by the Tafel method. The lead cathode was placed in 20\% sulfuric acid and surrounded by a sheet of lead. It was made the anode using current density of 0.02 ampere per cm.\textsuperscript{2} and the current was allowed to flow for five minutes. A chocolate brown layer of lead oxide appeared on the surface of the lead used as anode. The polarity was then reversed and the current again allowed to run for five minutes. The lead oxide was reduced to spongy lead. The cycle was repeated and at the end of the second cycle a third was begun but the cathode was left in the oxidized condition. It was washed thoroughly with distilled water before using.

The porous cup was completely submerged in 20\% sulfuric acid each time before using for at least one hour, or if not using acid catholytes, in the solution in which it was to be used.

The isolation of the expected hydrazines was attempted by making derivatives. Benzaldehyde purified by washing with sodium bicarbonate solution and fractionating under an atmosphere of nitrogen, 2,4-dichlorobenzaldehyde, benzenesulfonylchloride, benzoyl chloride and phenyl isothiocyanate were tried. Also a basic solution of one of the catholytes was distilled, the distillate made acidic with hydrochloric acid and evaporated to dryness.
Titration of an aliquot portion of the catholyte with standardized iodine in the presence of sodium bicarbonate was also used. Siggia suggests 0.0005 to 0.001 mole of the hydrazine be used for the titration which is acidified with dilute sulfuric acid and one gram sodium bicarbonate added. The equation for the reaction is

$$\text{CH}_3\text{NNH}_2\cdot\text{H}_2\text{SO}_4 + 2\text{I}_2 + 5\text{NaHCO}_3 \rightarrow \text{CH}_3\text{I} + 3\text{NaI} + \text{Na}_2\text{SO}_4 + 5\text{CO}_2 + 5\text{H}_2\text{O} + \text{N}_2$$

This method was found to be sensitive to one per cent using hydrazine itself as a control and under the conditions at which we worked and was sufficiently accurate for our purposes. Siggia claims that this method is applicable to all hydrazines and can be used for quantitative purposes for all hydrazines.

**Experimental Technique**

A typical reduction was carried out using the following procedure. A porous cup which was to be used was removed from the acid or other wash, and rinsed with distilled water. The surfaces of all solid single metal cathodes (except thin electroplates) were cleaned by anodization.

A weighed amount of the organic compound to be reduced, and any promoter, were placed in the cup into which there was poured sufficient catholyte to fill completely the space left in the cup after the rubber stopper holding the cathode, condenser, Luggin capillary, and stirrer had been placed in position and the desired temperature reached. The rubber stopper was fitted snugly to the cap.

A beaker containing the anode was placed in position in an ice bath with the anode surrounding the cup which rested on the bottom of the beaker.
Anolyte was then poured quickly into the anode compartment so that the liquid levels of anolyte and catholyte were the same.

The current was turned on and adjusted quickly to the desired value. An amper density of 0.0311 amper per square centimeter was used in most experiments since the cathodes which were constructed to fit into the porous cups were fifty-eight square centimeters in area. The amperage used was 1.8 amperes.

The current and the voltage across the cell were recorded every hour. In some cases the cathodic voltage was also recorded every hour.

At the end of a run, the porous cup containing the catholyte was detached from the rubber stopper and the contents poured into a beaker. The cathode and cup were washed with distilled water and the washings added to the catholyte in the beaker.

**Experimental Details for Each of Electroreductions**

Each electroreduction will be discussed separately in the following pages but a table is included which summarizes important features of all the reductions.
<table>
<thead>
<tr>
<th>No.</th>
<th>Compound</th>
<th>Cathode</th>
<th>Catholyte</th>
<th>Anode</th>
<th>Anolyte</th>
<th>Ampere-hours Used</th>
<th>Remarks</th>
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</thead>
<tbody>
<tr>
<td>I</td>
<td>6 gm NO₂</td>
<td>Tinned</td>
<td>NaOOCCH₃</td>
<td>LEAD</td>
<td>H₂SO₄</td>
<td>8.63</td>
<td></td>
</tr>
<tr>
<td></td>
<td>CH₃N—COOET</td>
<td>Copper</td>
<td>HOOCCCH₃</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>II</td>
<td>4 gm NO₂</td>
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<td></td>
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<tr>
<td></td>
<td>CH₃N—COOET</td>
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<td></td>
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<td></td>
</tr>
<tr>
<td>III</td>
<td>4 gm NO₂</td>
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<td>10% H₂SO₄</td>
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<tr>
<td></td>
<td>CH₃N—NO₂</td>
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<td>Ni</td>
<td>10% HCl</td>
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<td>8</td>
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<tr>
<td>IV</td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td>1.51</td>
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</tr>
<tr>
<td>V</td>
<td></td>
<td></td>
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<td>6.97</td>
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</tr>
<tr>
<td>VI</td>
<td></td>
<td></td>
<td>Ni</td>
<td>10% HCl</td>
<td></td>
<td>9.0</td>
<td></td>
</tr>
<tr>
<td>VII</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>7.65</td>
<td>0.1000 gm SnCl₂ as catalyst</td>
</tr>
<tr>
<td>VIII</td>
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<td>Tinned</td>
<td></td>
<td></td>
<td></td>
<td>6.3 amps.</td>
<td></td>
</tr>
<tr>
<td>IX</td>
<td></td>
<td>Copper</td>
<td></td>
<td></td>
<td></td>
<td>8.3</td>
<td></td>
</tr>
<tr>
<td>X</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.8</td>
<td></td>
</tr>
<tr>
<td>XI</td>
<td></td>
<td></td>
<td>Ni</td>
<td>10% H₂SO₄</td>
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<td></td>
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<tr>
<td>XII</td>
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<td></td>
<td>20% HCl</td>
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<td>Circuit breaks</td>
</tr>
<tr>
<td>XIII</td>
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<td></td>
<td></td>
<td>10% HCl</td>
<td>11 amps.</td>
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</tr>
<tr>
<td>XIV</td>
<td></td>
<td>Pb</td>
<td>10% HCl</td>
<td></td>
<td></td>
<td>6.4 amps.</td>
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</table>
The catholyte used was 10 grams of crystalline sodium acetate dissolved in 30 ml. of acetic acid and 70 ml. of water. To it was added 6 g. (0.0405 mole) of the nitrocarbamate. The theoretical amount of current to be passed through the cell in reductions I and II was 6.53 ampere hours.

\[
\frac{6}{148} = \frac{\text{Amt. current}}{6} = 0.244 \text{ faradays}
\]

\[0.244 \times 26.8 = 6.53 \text{ ampere hours.}\]

In I the amount of current used was 8.63 ampere hours. One and eight-tenths amperes were applied for three hours. The readings of the voltmeter across the cell were:

- Zero hour: 3.40 volts
- First hour: 3.60 volts
- Second hour: 3.65 volts
- Third hour: 3.80 volts

Then at the end of the third hour the amperage was reduced to 1.1 amperes thus giving a lower current density and greater chance for reduction to occur before evolution of hydrogen. The voltage reading for the next two hours was:

- Fourth hour: 3.4 volts
- Fifth hour: 3.5 volts

**Weight coulometer plate after passage of current** 23.0955 gms.

**Weight coulometer plate before passage of current** 12.8653 gms.

**Wgt. copper deposited** 10.2302 gms.
\[
\frac{10.2302}{\text{equiv. wt. Cu}} = \text{No. amp. hrs.}\]

\[
\text{no. amp. hrs.} \times \frac{10.2302}{31.8} \times 26.8 = 8.63 \text{ ampere hours or a } 32\% \text{ excess above the theoretical.}
\]

It was also found that the tinned copper cathode lost 0.0152 gram during the passage of the current.

Throughout the length of the experiment, gas was evolved at the cathode but faster after the third hour. Two and eight-tenths grams of unreacted starting material were recovered from the catholyte which had become slightly pink after the passage of current.

As H. J. Backer had claimed that the hydrazines of the compounds he reduced electrolytically were isolated as aromatic aldehyde derivatives, benzaldehyde was added to a portion of the catholyte with no appearance of a derivative. The benzaldehyde was impure and on the assumption that this might be the reason that no derivative appeared, the benzaldehyde was purified by washing with 5% sodium bicarbonate (used petroleum ether to break the emulsion which was formed), drying with anhydrous potassium carbonate and distilling under reduced pressure in an atmosphere of nitrogen (Temperature 850-860, pressure 27 mm. of mercury).

This purified benzaldehyde gave no derivative either.

The catholyte, after electrolysis, decolorized potassium permanganate solution, whereas the original solution did not.

II. This electroreduction was carried out under the same conditions as before except a probing electrode was used to measure the voltage of the cathode.
The total amount of current used as ascertained from the copper coulometer was 7.2 ampere hours. The tin cathode lost 0.1492 g. in weight. The readings of the voltmeter and the probing electrode indicate the occurrence of a reduction. The readings of the ammeter, voltmeter, and probing electrode during the passage of current are given in the following table.

<table>
<thead>
<tr>
<th>Hours</th>
<th>Ammeter (Ampères)</th>
<th>Voltmeter (Volts)</th>
<th>Probing Electrode (Volts)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.8</td>
<td>3.5</td>
<td>1.3205</td>
</tr>
<tr>
<td></td>
<td>Without organic compound</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>1.8</td>
<td>3.10</td>
<td>0.5438</td>
</tr>
<tr>
<td>1</td>
<td>1.8</td>
<td>3.20</td>
<td>0.5200</td>
</tr>
<tr>
<td>2</td>
<td>1.8</td>
<td>3.40</td>
<td>0.5478</td>
</tr>
<tr>
<td>3</td>
<td>1.3</td>
<td>3.00</td>
<td>0.5526</td>
</tr>
<tr>
<td>4</td>
<td>1.3</td>
<td>3.05</td>
<td>0.5995</td>
</tr>
<tr>
<td>5</td>
<td>1.3</td>
<td>3.40</td>
<td>1.0067</td>
</tr>
<tr>
<td>6</td>
<td>1</td>
<td>3.50</td>
<td>1.5000</td>
</tr>
</tbody>
</table>

At about five and a half hours, a copious evolution of gas was noticed.

The catholyte was a greyish green and no unreacted ethyl-N-nitro-N-methylcarbamate was recovered but there was a trace of metallic tin in the catholyte.

Benzaldehyde and enough alcohol to give a homogeneous solution were added to an aliquot of the catholyte, but no precipitate appeared. 2,4-Dichlorobenzaldehyde was also tried. The 2,4-dichlorobenzaldehyde was dissolved in alcohol and added to a solution neutralized to a
phenolphthalein end-point of the catholyte but again there was no precipitate. Other compounds which were tried for making a derivative of a hydrazine were benzoyl chloride, benzenesulfonylchloride, and phenyl isothiocyanate.

Twenty-five mls. of the catholyte were made basic and extracted with ether. Distillation of the ether left a few drops of oil. The remainder of this aliquot was then distilled and the fraction boiling between 86°C to 99-1/2°C was collected and found to be basic to litmus. The collected distillate was acidified to litmus paper with hydrochloric acid and evaporated on the steam bath. A residue which weighed 0.4 g. remained and was in the form of yellow plates and melted at 173°C-174°C. A small amount of this yellow solid dissolved in water decolorized potassium permanganate solution.

The volume of catholyte and washings was 110 ml. or the amount of solid in the total volume would be \( \frac{110 \times 0.4}{25} = 1.76 \) gm. indicating a possible yield of 32% N-carbethoxy-N-methylhydrazine.

III. An electroreduction was tried under the same conditions as for I and II using 4 grams of N-methyl-N-nitrosoamine. The theoretical amount of current to reduce this compound is 8.45 ampere-hours.

The actual amount of current used was 9.6 ampere-hours.

The following readings of the voltmeter, ammeter, and probing electrode were noted:
The catholyte and washings had a volume of 110 ml., and were a light milky gray and reduced permanganate readily. They also gave a negative test with the diphenylamine reagent for the $N$-nitro grouping.

Thirty cc. of the catholyte were titrated to a phenolphthalein end-point with 10% potassium hydroxide then two extra drops of the 10% potassium hydroxide were added. A small amount of inorganic precipitate, stannous hydroxide, was filtered off. Then acetic acid was added until a pH of 4 was reached. To this prepared catholyte was added 15 cc. of ethanol and heated on the steam bath but again more precipitate appeared which was inorganic. To the filtrate was added 1.53 g. of benzaldehyde and heated on the steam bath, but no precipitate appeared.

To another 30 cc. of the catholyte was added potassium hydroxide until no more precipitate appeared. This precipitate was probably tin
hydroxide. The filtrate was then distilled and three fractions were arbitrarily collected, the cuts were made at 55°C, 86°C, and 100°C, but none of these fractions decolorized potassium permanganate.

It was decided at this time that a quantitative volumetric method for the determination of the hydrazine might be tried and the method of Siggia\(^{15}\) was chosen. The stoichiometric equation for the oxidation-reduction involved in this method is

\[
\text{CH}_3\text{NHNH}_2\text{H}_2\text{SO}_4 + 2\text{I}_2 + 5\text{NaHCO}_3 \rightarrow \text{CH}_3\text{I} + 3\text{NaI} + \text{Na}_2\text{SO}_4 + 5\text{CO}_2 + \text{N}_2
\]

Siggia suggests that 0.0005 to 0.001 mole of the hydrazine be used in the titration. The equation which was used to determine the percentage of hydrazine is

\[
\frac{\text{Ml. Iodine} \times \text{Normality iodine} \times \text{Molecular Wgt. Hydrazine} \times 100}{\text{Grams sample} \times 4000}
\]

The four thousand in this equation is composed of two figures multiplied together. The one thousand to have equivalent units and not millimoles and moles, the four since hydrazine is oxidized and thus to have the figures for iodine and hydrazine in normalities. From the percentage of hydrazine found can then be calculated the weight of hydrazine and the percentage conversion.

The iodine solution was standardized according to the method in Willard and Furman\(^{18}\)

\[
\text{Na}_2\text{AsO}_2 + \text{I}_2 + 3\text{NaHCO}_3 \rightarrow \text{Na}_2\text{HAsO}_4 + 2\text{NaI} + 3\text{CO}_2 + \text{H}_2\text{O}
\]

and starch indicator was used.\(^{19}\)

A blank on a known sample of hydrazine using the Siggia method showed that the accuracy was sufficient for our purposes. A titration
on an aliquot portion of the catholyte indicated a 2% yield of hydrazine.

IV. The electroreduction was repeated exactly as in III with the exception that only 1.51 ampere hours of current were used. The catholyte was a greyish color and there was some metallic tin suspended in it.

<table>
<thead>
<tr>
<th>Time</th>
<th>Ammeter</th>
<th>Voltmeter</th>
<th>Probing Electrode</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.8</td>
<td>3.10</td>
<td>0.5280</td>
</tr>
<tr>
<td>No depolarizer</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>1.8</td>
<td>2.7</td>
<td>0.4965</td>
</tr>
<tr>
<td>1/2 hr.</td>
<td>1.8</td>
<td>2.8</td>
<td>0.5575</td>
</tr>
<tr>
<td>1 hr.</td>
<td>1.1</td>
<td>2.65</td>
<td>0.5260</td>
</tr>
</tbody>
</table>

Titration of an aliquot by the Siggia method showed a 4.4% conversion of the nitroamine to the hydrazine.

The cathode had lost 0.5489 g. of tin.

V. The same electroreduction as in III and IV was repeated using 6.97 ampere hours of current. At the end of the electroreduction the catholyte was a pure milky white. The yield as shown by titration was 18%.
<table>
<thead>
<tr>
<th>Hours</th>
<th>Amperage</th>
<th>Voltmeter</th>
<th>Probing Electrode</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2.5</td>
<td>3.1</td>
<td>0.8805</td>
</tr>
<tr>
<td>0</td>
<td>2.5</td>
<td>2.9</td>
<td>0.5770</td>
</tr>
<tr>
<td>1</td>
<td>2.5</td>
<td>3.5</td>
<td>0.8559</td>
</tr>
<tr>
<td>2</td>
<td>1.5</td>
<td>3.2</td>
<td>0.9105</td>
</tr>
<tr>
<td>3</td>
<td>1.1</td>
<td>3.4</td>
<td>0.940</td>
</tr>
<tr>
<td>4</td>
<td>0.5</td>
<td>3.2</td>
<td>0.924</td>
</tr>
<tr>
<td>5</td>
<td>0.5</td>
<td>3.2</td>
<td>0.942</td>
</tr>
<tr>
<td>6</td>
<td>0.3</td>
<td>3.2</td>
<td>0.900</td>
</tr>
<tr>
<td>7</td>
<td>0.5</td>
<td>3.2</td>
<td>0.942</td>
</tr>
<tr>
<td>8</td>
<td>0.3</td>
<td>3.1</td>
<td>0.9030</td>
</tr>
<tr>
<td>9</td>
<td>0.3</td>
<td>3.2</td>
<td>0.912</td>
</tr>
</tbody>
</table>

Fifty ml. of the catholyte were made basic and distilled to dryness into hydrochloric acid solution. The distillate did not reduce potassium permanganate solution but the solid remaining in the pot did reduce potassium permanganate solution.

A calculation of the titration using iodine was made assuming that the substance titrated was stannous ion but this showed that 2.25 grams of tin should have been present as stannous ion whereas only 0.0707 g. of tin was lost from the cathode.

VI. In this electroreduction an anodized nickel cathode (with an area of 61 cm²) was used, with 10% hydrochloric acid as the catholyte. The anode was lead and the anolyte 20% sulfuric acid. Four grams of N-methyl-N-nitroamine were added to the cathode compartment.
Eight ampere-hours of current were used or a current of two amperes for four hours. The catholyte was pale green and had a volume of 153 ml. Titration by the method of Siggia on 2.9 ml. gave a value for 20.2% conversion to the hydrazine.

The remaining catholyte was evaporated to dryness and a green solid remained \((\text{NiCl}_2 \cdot 6\text{H}_2\text{O})\). Concentrated potassium hydroxide solution was added to this solid and the solution extracted with ether. The ether extract did not reduce the iodine solution.

VII. The reduction as in VI was repeated. The total current used was 9.0 ampere-hours. The following current and voltage readings were obtained:

<table>
<thead>
<tr>
<th>Hours</th>
<th>Ammeter Reading</th>
<th>Voltmeter Reading</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>No depolarizer</td>
<td>3 amps.</td>
<td>3.5</td>
</tr>
<tr>
<td>0</td>
<td>(1.1)</td>
<td>3.2</td>
</tr>
<tr>
<td>1/2 hr.</td>
<td>2.5</td>
<td>3.2</td>
</tr>
<tr>
<td>1 hr.</td>
<td>2</td>
<td>3.15</td>
</tr>
<tr>
<td>2 hrs.</td>
<td>2</td>
<td>3.5</td>
</tr>
<tr>
<td>2-1/4 hrs.</td>
<td>1.5</td>
<td>3.2</td>
</tr>
<tr>
<td>3 hrs.</td>
<td>1.1</td>
<td>3.1</td>
</tr>
<tr>
<td>4 hrs.</td>
<td>1.1</td>
<td>3.2</td>
</tr>
<tr>
<td>5-1/4 hrs.</td>
<td>1.1</td>
<td>3.2</td>
</tr>
</tbody>
</table>

A titration with iodine indicated a 19.3% yield.
VIII. Repeated the reduction using the nickel cathode as in VI and VII. This time added to the catholyte 0.1000 g. of stannous chloride as catalyst.

Seven and sixty-five hundredths ampere-hours of current was used. The nickel cathode lost 0.078 g. of weight. The readings of the ammeter and voltmeter were as follows:

<table>
<thead>
<tr>
<th>Hours</th>
<th>Ammeter (Amperes)</th>
<th>Voltmeter (Volts)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2.5</td>
<td>3.6</td>
</tr>
<tr>
<td>No depolarizer but SnCl₂</td>
<td>2.0</td>
<td>3.4</td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>3.1</td>
</tr>
<tr>
<td></td>
<td>1.1</td>
<td>2.9</td>
</tr>
<tr>
<td>0</td>
<td>2</td>
<td>3.1</td>
</tr>
<tr>
<td>depolarizer</td>
<td>1.5</td>
<td>3.4</td>
</tr>
<tr>
<td>1</td>
<td>1.5</td>
<td>3.6</td>
</tr>
<tr>
<td>2 hrs.</td>
<td>1.5</td>
<td>3.6</td>
</tr>
<tr>
<td>3 hrs.</td>
<td>1.5</td>
<td>3.6</td>
</tr>
<tr>
<td>4 hrs.</td>
<td>1.5</td>
<td>3.8</td>
</tr>
<tr>
<td>5 hrs.</td>
<td>1.0</td>
<td>3.5</td>
</tr>
<tr>
<td>6 hrs.</td>
<td>1.0</td>
<td>3.5</td>
</tr>
</tbody>
</table>

A copious evolution of gas occurred throughout the time of the experiment. The catholyte was an off white color and had a volume of 100 ml. A titration showed a yield of 10.9% but there was some stannous ion present which would react with the iodine.
IX. In this electroreduction, the same conditions as in III were used, except that the catholyte was 10% hydrochloric acid. The current used was 6.3 ampere hours.

There was gaseous evolution throughout this experiment. The catholyte was colorless but had a white solid in suspension. A titration showed a yield of 12.3%.

<table>
<thead>
<tr>
<th>Hours</th>
<th>Ammeter (Ampere)</th>
<th>Voltmeter (Volts)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.8</td>
<td>3.1</td>
</tr>
<tr>
<td>No depolarizer</td>
<td>1.8</td>
<td>2.9</td>
</tr>
<tr>
<td>3/4</td>
<td>1.25</td>
<td>2.9</td>
</tr>
<tr>
<td>4-3/4</td>
<td>1.25</td>
<td>2.9</td>
</tr>
</tbody>
</table>

X. An electroreduction using the conditions of IX was performed but only 1.8 ampere-hours of current were used. A titration on the catholyte indicated a yield of 4.93%.

XI. A nickel cathode in 10% sulfuric acid as the catholyte was tried. The total current passed through the cell was 8.2 ampere-hours.
<table>
<thead>
<tr>
<th>Hours</th>
<th>Ammeter (Ampères)</th>
<th>Voltmeter (Volts)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.8</td>
<td>3.2</td>
</tr>
<tr>
<td>0</td>
<td>1.8</td>
<td>2.9</td>
</tr>
<tr>
<td>2-1/4</td>
<td>1.5</td>
<td>3.0</td>
</tr>
<tr>
<td>3</td>
<td>1.1</td>
<td>3.0</td>
</tr>
<tr>
<td>5</td>
<td>0.8</td>
<td>3.0</td>
</tr>
<tr>
<td>6</td>
<td>0.8</td>
<td>3.0</td>
</tr>
</tbody>
</table>

The catholyte was light grey. A titration indicated a yield of 16.8%.

XII. A nickel cathode was tried using 20% hydrochloric acid as the catholyte. The same anode and anolyte were used as in the previous experiments. The ammeter burned out after an hour but the catholyte was titrated and a yield of 10.6% was indicated.

XIII. The experiment of XII was repeated. A large evolution of hydrogen was observed throughout the experiment. A titration indicated a yield of 18.2%.

<table>
<thead>
<tr>
<th>Hours</th>
<th>Ammeter</th>
<th>Voltmeter</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.8</td>
<td>3</td>
</tr>
<tr>
<td>5</td>
<td>1.5</td>
<td>3</td>
</tr>
<tr>
<td>6</td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td>6-1/2</td>
<td>1</td>
<td>2.9</td>
</tr>
</tbody>
</table>

XIV. A lead cathode was prepared and anodized for this experiment and used in a catholyte of 10% hydrochloric acid.
<table>
<thead>
<tr>
<th>Hours</th>
<th>Ammeter</th>
<th>Voltmeter</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.8</td>
<td>3.5</td>
</tr>
<tr>
<td>No depolarizer</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>1.8</td>
<td>2.7</td>
</tr>
<tr>
<td>1-1/2</td>
<td>1.8</td>
<td>2.9</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>3.0</td>
</tr>
</tbody>
</table>

The current used was 5.3 amperes hours. The catholyte was colorless and the brown anodized cathode had been reduced and was silvery. A titration indicated a yield of 11.5%.

The catholyte from several of these reductions using nickel was evaporated to dryness. The solid remaining was not melted nor did it burn at red heat and the reducing power of the catholyte resided in this solid. This indicates that the compound which reacted with the oxidizing agent was inorganic and no reduction to a hydrazine had occurred since organic compounds all burn with only a very few well-known exceptions (as carbon tetrachloride) and hydrazines are not in this category.

Part III. Use of Polarographic Method

The polarographic method has been used not only to determine the potential at which reductions occur, but also for reduction of a macro sample using a mercury pool as the cathode. The possibilities of the method are well expressed by Lingane, Swain, and Fields:

"Electrode potential is the primary factor which determines the success or failure of electrolytic methods."

"From a preliminary polarographic investigation of a projected starting material under widely diverse conditions of solution, composition,
pH, temperature, etc., the feasibility of, and optimum conditions for, a large scale electrolytic preparation with practically quantitative yield usually can be determined readily, regardless of whether or not the electrode reaction is reversible. Since solid microelectrodes can be used in the polarographic method, the most satisfactory electrode material for a given reaction can be found.

Inasmuch as no reduction of the N-methyl-N-nitroamine to the hydrazine was effected electrolytically and to use a method which seemed less dependent on chance, the polarographic method was tried.

The Fischer electropode was used in the polarographic analyses in conjunction with an H-type cell and a saturated calomel reference electrode. The buffers used were Clarke and Lubs buffers prepared as described in Willard, Merritt and Dean, "Instrumental Methods of Analysis". Gelatin was tried as a suppressor so that no maxima would appear in the curves but it was found that maxima did not occur even when the gelatin was not used, probably because the N-methyl-N-nitroamine acted as a suppressor.

It was found that at a low pH the hydrogen maximum obscured the reduction wave but at a pH greater than six the wave due to reduction was visible but at higher pH's, i.e. pH 9, the wave for the reduction of the organic compound ran into the wave for the reduction of the alkali metal ions.

A plot of \( \log \frac{1}{i_d-i} \) vs. voltage gives a straight line and in a reversible reduction-oxidation system will give the number of electrons exchanged. This was done for the data of polarogram IX-A and a straight line (graph I) was obtained but this is not significant however, since
a straight line may also be obtained when a reduction is not thermodynamically reversible. The number of electrons taking part in the reduction cannot be found from graph I.

Graph No. 2 is one of pH vs. half-wave potential and gives a straight line. The half-wave potential shifts to more negative values of applied voltage with increasing pH. This is an indication that the same compound is the end product at all pH's. The theoretical expression for the half-wave potential is

$$E_{1/2} = E_0 + \frac{0.0591}{n} \cdot \text{pH}$$

and a straight line could be obtained in graph No. 2 only if n were the same in all the experiments included in the graphs since the number given by $\frac{0.0591}{n}$ is the slope of the line and n must be the same in all cases in order for the points to be along the same straight line.

Controlled potential reduction was also tried, the reduction carried out at the voltage indicated by the polarograms. Different mercury pools were used as cathode and anode. Difficulties were met since too little material had to be employed and the hydrazine could not be isolated. Controlled potential reductions using nitroamines insoluble in water might resolve the separation difficulty. Another solution would be to find the appropriate electrodes using microelectrodes for the polarograms, after the $E_{1/2}$ has been found using the dropping mercury electrode, and carrying out an electroreduction with these metals as the cathode. In this manner the electroreduction could be conducted faster and a larger amount of starting material could be used.

Experimental: A. Polarographic Investigation of N-methyl-N-nitroamine

In 100 ml. of distilled water were dissolved 0.0611 gms. of
N-methyl-N-nitroamine so that 5 ml. of this solution diluted to 50 ml. for a polarogram would give a solution which was 0.008 molar. The gelatin solution was prepared by dissolving 0.2 g. of gelatin in enough water to give a volume of 100 ml., and it was intended that 2 ml. of this stock solution be used for each polarogram thus giving a solution 0.008% in gelatin. It was found that gelatin was unnecessary.

The H-type cell\(^26\) which was used for all the investigations described in this section was a standard type and was used in conjunction with a standard calomel electrode and a dropping electrode. This cell was furnished with a gas inlet tube which was used to flush out all oxygen with nitrogen before each polarogram.

The Fischer Electropode was standardized using a 10,000 ohms resistance. The following readings were obtained.
<table>
<thead>
<tr>
<th>Applied Voltage</th>
<th>Sensitivity</th>
<th>Ammeter Reading</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>5x</td>
<td>98</td>
</tr>
<tr>
<td>0.1</td>
<td>10x</td>
<td>50.5</td>
</tr>
<tr>
<td>0.1</td>
<td>20x</td>
<td>25.8</td>
</tr>
<tr>
<td>0.1</td>
<td>50x</td>
<td>10.5</td>
</tr>
<tr>
<td>0.1</td>
<td>100x</td>
<td>5.2</td>
</tr>
<tr>
<td>0.1</td>
<td>200x</td>
<td>2.7</td>
</tr>
<tr>
<td>0.30</td>
<td>20x</td>
<td>77.8</td>
</tr>
<tr>
<td>0.30</td>
<td>50x</td>
<td>31.6</td>
</tr>
<tr>
<td>0.30</td>
<td>100x</td>
<td>15.8</td>
</tr>
<tr>
<td>0.30</td>
<td>200x</td>
<td>7.8</td>
</tr>
<tr>
<td>0.30</td>
<td>500x</td>
<td>3.2</td>
</tr>
<tr>
<td>0.50</td>
<td>50x</td>
<td>52.6</td>
</tr>
<tr>
<td>0.50</td>
<td>100x</td>
<td>26.5</td>
</tr>
<tr>
<td>0.50</td>
<td>200x</td>
<td>13.2</td>
</tr>
<tr>
<td>0.50</td>
<td>500x</td>
<td>5.2</td>
</tr>
<tr>
<td>1</td>
<td>100x</td>
<td>52.5</td>
</tr>
<tr>
<td>1</td>
<td>200x</td>
<td>26.2</td>
</tr>
<tr>
<td>1</td>
<td>500x</td>
<td>10.5</td>
</tr>
</tbody>
</table>

At 5x it was found that each deflection corresponded to a passage of \(1.02 \times 10^{-7}\) amperes of current. By Ohm's law \(I = \frac{E}{R}\) and \(\frac{0.1}{10,000} = 1 \times 10^{-5}\) amperes.

\[
\frac{1 \times 10^{-5}}{98} = 1.02 \times 10^{-7} \text{ amperes/deflection}
\]
I. Into a 50 ml. volumetric flask were placed 20 ml. of 0.2 N. hydrochloric acid solution, 20 ml. of 0.2 N. potassium chloride, 5 ml. of the stock N-methyl-N-nitroamine, and 2 ml. of the stock gelatin solution and diluted to the mark with distilled water. This solution was added to the electrolysis cell and nitrogen bubbled through it for 20 minutes through the inlet tube. The pH of this solution was about 1.3.

A polarogram was taken of this solution from 0 to 2 volts. The readings are versus the normal calomel electrode and are shown in polarogram number I.

The maximum in this curve is due to hydrogen.

II. Purification of Alcohol

It was decided to run the remainder of the polarograms in an alcoholic medium and blanks were run of absolute ethyl alcohol (Polarogram number II) and on Merck acetone free methyl alcohol (Polarogram number III). In both cases the polarogram indicated the presence of reducible substances.

The absolute alcohol was run through a 100 ml. buret containing silica gel but the polarogram of this alcohol still showed maxima (Polarogram number IV).

The absolute alcohol was then treated with magnesium turnings (10 gms. magnesium to 1950 ml. absolute alcohol) and refluxed, which rid the alcohol

\[ \text{Mg} + \text{C}_2\text{H}_5\text{OH} \rightarrow \text{Mg(C}_2\text{H}_5)_2 \]

\[ \text{Mg(O}_2\text{C}_2\text{H}_5)_2 + 2\text{H}_2\text{O} \rightarrow \text{Mg(OH)}_2 + 2\text{C}_2\text{H}_5\text{OH} \]

of any water present by precipitating it out in the form of magnesium hydroxide. The treated alcohol was then fractionated using a three foot, silvered, vacuum jacketed column filled with glass helices. A fraction
was discarded (20 cc.) which boiled below 60°C. and had a strong aldehydic odor, and a fraction boiling between 75°-77°C. was also discarded. The fraction collected boiled at 78°C. and its polarogram showed that the reducible substances had been substantially eliminated (Polarogram number V).

III. Ten ml. of 0.6 N. hydrochloric acid solution, 10 ml. of 0.6 N. potassium chloride solution, 25 ml. of the ethyl alcohol and 5 ml. of the stock N-methyl-N-nitroamine were added to the H-type cell. A polarogram was taken and showed the same characteristics as polarogram number I; i.e., a maximum due to hydrogen beginning at about 1 volt (Polarogram number VI).

A polarogram of the medium used above (25 ml. of ethyl alcohol, 10 ml. of 0.6 N. hydrochloric acid solution, 10 ml. of 0.6 N. potassium chloride and 5 ml. of distilled water) showed the same maximum (Polarogram number VII).

IV. Polarogram number VIII was not buffered but was run to see where the reduction occurred. Twenty-five ml. of alcohol, 10 cc. of 0.6 N. potassium chloride and 5 ml. of the stock N-methyl-N-nitroamine solution were diluted to 50 ml. in a volumetric flask using distilled water. The polarogram shows reduction occurred at the voltage at which hydrogen is liberated in the acidic solutions used so far and was masked by this. The graph of this polarogram also indicates that the alcohol (see polarogram number V) gave an unevenness to the curves.

Because of this solvent effect polarograms numbers IX and IXa were run using 10 ml. of 0.6 N. potassium chloride and 5 ml. of the standard solution of N-methyl-N-nitroamine diluted to 50 ml. with distilled water.
As is evident from the graphs of these two polarograms, the unevenness due to the solvent has been eliminated. From the graph of polarogram number IXa, it was found that the half-wave potential was 1.26 volts and the diffusion current was $22.5 \times 1.07 \times 10^{-7} = 2.4 \times 10^{-6}$ amperes by using the method for measurement of diffusion current for ill-defined polarographic waves.

V. Eight ml. of 0.6 N. sodium hydroxide, 10 ml. of 0.6 N. potassium biphthalate, and 5 ml. of the stock solution of N-methyl-N-nitroamine were diluted to 50 ml. with distilled water. The pH of this solution was approximately 6. A wave occurred indicating a reduction with an $E_{1/2}$ close to that of the unbuffered solutions and also a hydrogen maximum beginning at about 1.5 volts. The graph of this polarogram is labeled Polarogram number X.

VI. Polarogram number XI was taken at a pH of 8. Nine and four-tenths ml. of 0.6 N. sodium hydroxide, 10 ml. of 0.6 N. monopotassium phosphate, and 5 ml. of the N-methyl-N-nitroamine solution were diluted to 50 ml. A wave indicating reduction is visible but the half-wave potential is increased from that at pH of 6. A greater increase in the half-wave potential is evident at a pH of 9 (Polarogram number XII). This polarogram was run using 4.3 ml. of 0.6 N. sodium hydroxide, 20 ml. of 0.3 N. boric acid in 0.3 N. potassium chloride, and 5 ml. of the N-methyl-N-nitroamine.

VII. To find a pH at which the end of reduction as shown by the wave in the polarogram was not obscured, polarograms were run at pH 6.3, 6.4, 6.6, and 7.0 whose corresponding graphs are numbered polarograms numbers XIII, XIV, XV and XVI respectively.
To make the solutions the following quantities of 0.6 N. NaOH and of 0.6 N. monopotassium phosphate were added to 5 ml. of the stock solution of N-methyl-N-nitroamine and diluted to 50 ml. in a volumetric flask using distilled water.

<table>
<thead>
<tr>
<th>pH</th>
<th>NaOH</th>
<th>KH$_2$PO$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.3</td>
<td>2 ml.</td>
<td>10 ml.</td>
</tr>
<tr>
<td>6.4</td>
<td>2.5 ml.</td>
<td>10 ml.</td>
</tr>
<tr>
<td>6.6</td>
<td>3.56 ml.</td>
<td>10 ml.</td>
</tr>
<tr>
<td>7</td>
<td>5.93 ml.</td>
<td>10 ml.</td>
</tr>
</tbody>
</table>
Graph No. 1

\[ E = E_{y_2} - \frac{0.0591}{n} \log \frac{L}{L_d - L} \]

\[ \frac{n}{0.0591} = \frac{A \log \frac{L}{L_d - L}}{AE} \]

\[ \frac{n}{0.0591} = \frac{0.583 - (-0.82)}{1.36 - 1.12} = \frac{1.403}{0.24} = 5.83 \]
Polarogram No. 1

Plotted at 5x - Each deflection is equivalent to $1.02 \times 10^{-7}$ amperes of current.
Plotted at 5x - Each deflection is equivalent to $1.02 \times 10^{-7}$ amperes of current
Plotted at 5x - Each deflection is equivalent to $1.02 \times 10^{-7}$ amperes of current.
Plotted at 5x - Each deflection is equivalent to $1.02 \times 10^{-7}$ amperes of current
Polarogram No. 5

Plotted at 5x - Each deflection is equivalent to $1.02 \times 10^{-7}$ amperes of current
Polarogram No. 6

Plotted at 5x - Each deflection is equivalent to $1.02 \times 10^{-7}$ amperes of current
Polarogram No. 7

Plotted at 5x - Each deflection is equivalent to 1.02 \times 10^{-7} \text{ amperes of current}
Plotted at 5x - Each deflection is equivalent to $1.02 \times 10^{-7}$ amperes of current.
Polarogram No. 9

Plotted at 5x - Each deflection is equivalent to $1.02 \times 10^{-7}$ amperes of current
Polarogram No. 9a

Plotted at 5x - Each deflection is equivalent to $1.02 \times 10^{-7}$ amperes of current
Polarogram No. 10

Plotted at 5x – Each deflection is equivalent to $1.02 \times 10^{-7}$ amperes of current
Polarogram No. 11

Plotted at 5x - Each deflection is equivalent to $1.02 \times 10^{-7}$ amperes of current
Plotted at 5x - Each deflection is equivalent to $1.02 \times 10^{-7}$ amperes of current
Polarogram No. 13

Plotted at 5x - Each deflection is equivalent to $1.02 \times 10^{-7}$ amperes of current.
Polarogram No. 14

Plotted at 5x - Each deflection is equivalent to $1.02 \times 10^{-7}$ amperes of current
Polarogram No. 15

Plotted at 5x - Each deflection is equivalent to $1.02 \times 10^{-7}$ amperes of current.
Plotted at 5x - Each deflection is equivalent to 1.02 \times 10^{-7} amperes of current
B. Controlled Potential Reduction

The cell used for the preparative work was that described by Lingane, Swain and Fields.\textsuperscript{22} It is pictured in the diagram. The large compartment was constructed from a 500 ml. wide-mouthed Erlenmeyer flask. A coarse sintered glass disk, D, 4 cm. in diameter was sealed into the connecting tube between the two compartments and an agar plug containing the same electrolyte, potassium chloride, as the supporting electrolyte used in the cell was used at this point. This minimized interdiffusion of the two solutions. Both compartments were provided with gas inlet tubes T for removal of dissolved air with a stream of nitrogen.

A large pool of mercury, 68 cubic centimeters, on the bottom of the larger compartment was used as the cathode, and a smaller pool of mercury, 20 cubic centimeters, on the bottom of the smaller compartment served as the anode. With the exception of the substance to be reduced both compartments contained 0.12 N. potassium chloride as the supporting electrolyte.

A stirrer was mounted in the cathode compartment close to the mercury.
The potential of the large mercury cathode was measured against a standard calomel electrode using a 28 megohm Hickok vacuum tube voltmeter. A narrow U-tube, B, filled with saturated potassium chloride in a 3% agar gel served as a salt bridge between the standard calomel electrode and the mercury cathode. The tip of this bridge was placed within one millimeter of the mercury surface to minimize the amount of ohmic potential drop in the solution that is included in the measured cathode potential.

The voltage was taken from the d.c. house main which was set to deliver 12 volts, but a potentiometer-rheostat was used to maintain the measured cathode potential at the desired value. A calibrated ammeter was included in the circuit to measure the current through the cell.

The included diagram of the circuit incorporated all the features described above.
Experimental

1. A controlled potential reduction was tried at a pH of 6 using 250 ml. of 0.6 N monopotassium phosphate and 28.50 ml. of 0.6 N sodium hydroxide diluted to 450 ml. and 4 gms. of N-methyl-N-nitroamine.

<table>
<thead>
<tr>
<th>Hours</th>
<th>Cathodic Voltage</th>
<th>Milliamperes</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.40</td>
<td>65</td>
</tr>
<tr>
<td>3/4</td>
<td>1.40</td>
<td>65</td>
</tr>
<tr>
<td>1</td>
<td>1.40</td>
<td>75</td>
</tr>
<tr>
<td>6</td>
<td>1.30</td>
<td>50</td>
</tr>
<tr>
<td>11</td>
<td>1.30</td>
<td>50</td>
</tr>
</tbody>
</table>

After the sixth hour, the full 12 volts were used to keep up the cathodic voltage and current readings.

Neither starting material nor product could be isolated.
Bibliography

   Swann, ibid, 77, 459 (1940).
   Swann, ibid, 88, 103 (1945).


10. ibid, p. 224.


15. ibid, p. 171.


20. ibid, p. 265.


24. ibid, p. 182.

25. ibid, p. 271.

