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A STUDY OF THE ELECTROLYTIC REDUCTION OF PYRROLE

BY

DON RICHARD STREHLAU

A

THESIS

submitted to the faculty of the
SCHOOL OF MINES AND METALLURGY OF THE UNIVERSITY OF MISSOURI
in partial fulfillment of the work required for the

Degree of

MASTER OF SCIENCE, CHEMISTRY MAJOR

Rolla, Missouri

1942

Approved by


Assistant Professor of Organic Chemistry

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D. E. S.

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INTRODUCTION

A review of the chemical literature has shown that electro-organic methods compare favorably with purely chemical methods for certain syntheses belonging to the following general classes of reactions: coupling, oxidation, reactions with halogens, and reductions. Electro-organic methods have been used most successfully in synthesis by reduction. The chief advantage in using electrolytic reduction in preference to a chemical one is that it offers a more exact control of conditions, and consequently should give a higher yield and a purer product.

The advantages of this means of reduction suggested an investigation of its use in the synthesis of hydrogenated products of pyrrole, an unsaturated heterocyclic ring compound.

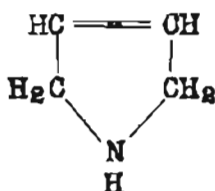
Two possible reduction products might result: a 2-5 dihydro pyrrole (pyrroline), and a tetra hydropyrrole (pyrrolidine), both of which are known and have been characterized. They have been produced by chemical and catalytic reduction in low yields from pyrrole.

The variable conditions to be studied in this investigation will include composition of the catholyte, cathode material, current density, time of electrolysis and temperature.

REVIEW OF THE PREVIOUS WORK

In 1883 Ciamician and Dennstedt⁽¹⁾ reported the reduction of pyrrole using zinc and acetic acid. The hydrogenated pyrrole was a great deal more basic than the parent substance. It was a colorless, water soluble oil of specific gravity 0.9097, boiling at 90-91° (748 mm.). It was also reported as fuming readily in moist air and absorbing carbon dioxide from the air.

By analysis, the investigators showed that the new product was a dihydrogenated pyrrole (pyrroline) presumably having the formula



No conclusive proof of this structure was offered.

The hydrochloric acid salt, $(\text{C}_4\text{H}_7\text{N})\text{HCl}$, and the chloroplatinic acid salt, $(\text{C}_4\text{H}_7\text{N})_2\text{H}_2\text{PtCl}_6$, were prepared as derivatives, melting at 173-174° and 182° with decomposition respectively. The substance was further characterized and shown to be a secondary amine giving a characteristic addition compound with methyl iodide, and a nitroso compound with nitrous acid.

The yield of base by this method was not at all

(1) Ciamician, L. and Dennstedt, M. *Berichte* Vol. 18, p. 1536 (1883)

satisfactory. Pyrroline was obtained in very small yields and in an impure form. During the reduction and isolation of products a great deal of ammonia was given off and most of the pyrrole was changed to a resin. It was observed that if the proportion of reactants to one another and the duration of the reduction were varied, no noteworthy increase in yield was obtained. Resinification and evolution of ammonia was increased with acid concentration and with duration of the reduction.

Knorr and Rabe⁽²⁾ later attempted to improve on the method of Ciamician and Dennstedt by using mineral acids and metals for the reduction mixture. Better yields of pyrroline were obtained and the method found to be applicable to the reduction of homologues of pyrrole as well. An 18 percent yield of pyrroline was the best reported - homologues of pyrrole gave better yields, since they were less sensitive than pyrrole to resinification.

In 1902 a patent was issued to Dennstedt⁽³⁾ on the electrolytic reduction of pyrrole to pyrroline. Almost quantitative reduction was claimed. A suspension of 40 grams of pyrrole in 80 ml. of 1-50 H_2SO_4 was electrolyzed

(2) Knorr, L. and Rabe, P. Berichte Vol. 34, p. 3491 (1901)

(3) Dennstedt, M. Deutsches Reich Patentschrift, No. 127-086 (1902)

at a current density of 0.01 amperes per sq. cm. Lead electrodes were used and the anolyte was separated from the catholyte by a porous clay cell. The patent stated it was not necessary to add acid to the catholyte during the run to replace that which was neutralized by the base produced, since the reduction proceeded as well in basic as in acid solution. The method of isolating the reduction product was not clearly stated, nor was any mention made of its identification.

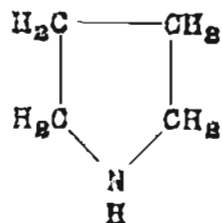
After the reduction, KOH was added to the catholyte in excess, and the mixture was steam distilled. The distillate was treated with HCl and evaporated to dryness. The yield was reported to be 50 grams of pyrrolidine hydrochloride. The free base was recovered from the HCl salt by adding 1-1 KOH solution and extracting with ether.

An allusion to the time of electrolysis was made by stating that the reduction was continued for a few hours after the cathode solution had become basic.

Next in sequence we find the attention of the investigating chemists turned toward the catalytic reduction of pyrrole. Putochin⁽⁴⁾ reported using nickel as a catalyst at 200°. During the hydrogenation, ammonia was evolved, indicating a good deal of decomposition. The product resulting in this case was pyrrolidine (tetra hydropyrrole)

(4) Putochin, H. J. Berichte 55 p. 2742 (1923)

having the formula



Like pyrroline, this compound was quite basic and gave the characteristic reactions of a secondary amine. It was a water soluble oil of specific gravity 0.8520 at 20°C. The yields by this method were very poor.

Zelinski and Iuriev⁽⁵⁾ carried out the reduction of pyrrole to pyrrolidine by passing pyrrole vapors slowly through a Pd asbestos catalyst at 160°. Again the yields reported were insignificant. N-methyl Pyrrole, in contrast, was hydrogenated quite easily under these conditions.

When he used a platinum oxide catalyst, Putochin⁽⁶⁾ claimed yields of 70-75% pyrrolidins. This reduction took place under pressure, at room temperature, in a solvent of a mixture of acetic acid and ethyl alcohol. After the first rapid absorption of hydrogen ceased, some HCl was added, and the reduction then resumed to completion.

Putochin's work could not be duplicated by Signaigo

(5) Zelinski, N. D. and Iuriev, I. K. *Berichte* Vol. 62 p. 2589-90 (1929)

(6) Putochin, N. J. *Chemical Abstracts* Vol. 25 p. 5995

and Adkins⁽⁷⁾, or by Cramer⁽⁸⁾. Their best results were obtained by using a nickel-kieselguhr catalyst at 200° with pressures of about 200 atmospheres. A 50 percent yield of pyrrolidine was reported. It was stated that pyrroles were more resistant to hydrogenation than any other unsaturated ring system encountered in their laboratory.

Sakurai⁽⁹⁾ reported reducing pyrrole electrolytically to pyrrolidine in 15 percent yields. Raney nickel and platinum black were used as catalysts by suspending them in the cathode solution. The reduction was carried out in a mixture of equal volumes of 10 percent sulfuric acid and alcohol. Lead and copper cathodes were used and the same yields reported for each. The yield of the reduction product could not be increased above a certain limit by increasing the time of electrolysis.

Sakurai's reductions were made at 30-34°C. with a current density of 0.1 amperes per square centimeter.

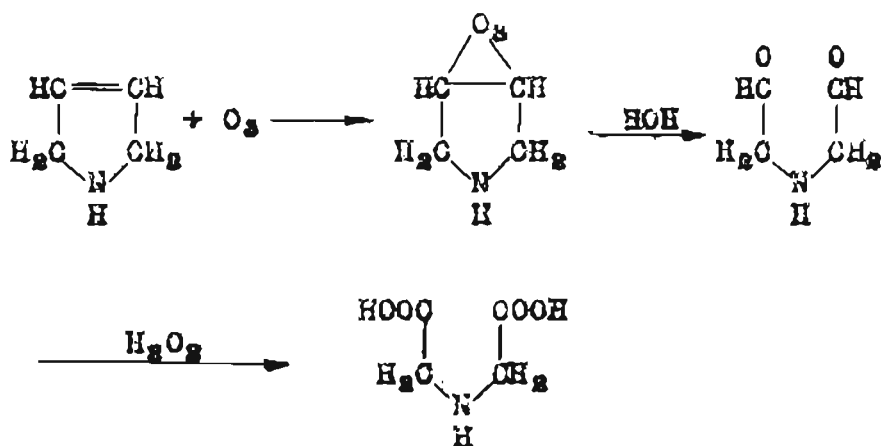
(7) Signaigo, F. and Adkins, H. J. Am. Chem. Soc. Vol. 52 p. 709-717 (1930)

(8) Cramer, H. and Adkins, H. J. Am. Chem. Soc. Vol. 52 p. 4349-4348 (1930)

(9) Sakurai, B. Bull. Chem. Soc. of Japan Vol. 11 p. 374-375 (1936)

Two grams of pyrrole dissolved in 100 cc. of electrolyte was electrolyzed for 6 hours.

Proof that a 2,5 dihydro pyrrole and not a 2,3 compound resulted from the reduction of pyrrole was conclusively brought out by Treibs and Dinelli⁽¹⁰⁾. Ozonization followed by oxidation with hydrogen peroxide produced imino diacetic acid as follows:



The imino diacetic acid was identified as the HCl salt melting at 235-237°C. and further as the diethyl ester melting sharply at 73°C.

(10) Treibs, A. and Dinelli, D. Liebigs Annalen Vol. 517 p. 170-173 (1935)

THEORY AND VARIABLES INVOLVED

The electrolytic reduction of an organic compound consists of two steps: (1) the formation of atomic hydrogen at the cathode; and (2) the interaction of the active hydrogen with the reducible substance with which it comes in contact⁽¹²⁾.

Molecular hydrogen has very little reducing power, and consequently the reducing power of a cathode must be ascribed to the hydrogen liberated on it while in the nascent state. According to the Mass Action Law, the reducing power of nascent hydrogen is proportional to its concentration. The potential difference between the cathode and the solution is also dependent on the concentration of the nascent hydrogen as can be shown as follows: The potential of the hydrogen electrode is given by the equation

$$(1) \quad e = RT \log \frac{P_{H_2}}{P_{H^+}}$$

P_{H_2} = electrolytic solution pressure

P_{H^+} = the osmotic pressure of the hydrogen ions in solution. However, $P = k_1 p$, in which k_1 is a constant and p is the pressure of the gaseous hydrogen in contact with the electrode and solution⁽¹³⁾.

By Henry's Law, p must be proportional to the concen-

(12) Creighton, H. The Electrochemical Reduction of Sugars
Trans. of the Electrochemical Soc. Vol. LXXV p. 290 (1939)

(13) Le Blanc Electro chemistry p. 183 (1907)

tration c_{H_2} of the molecular hydrogen in solution immediately on the electrode. The concentration of the molecular hydrogen must, in turn, be proportional to the square of the concentration of the nascent hydrogen on the electrode⁽¹⁴⁾ since the reaction is $2H = H_2$, and by the Mass Action Law, for equilibrium,

$$(c)^2 = k_2 c_{H_2}$$

The electrolytic solution pressure is, therefore, proportional to the concentration of the nascent hydrogen on the cathode, since

$$\frac{s}{P_{H_2}} = k_1 P = k_2 c = k_2 \frac{s}{c_{H^+}}$$

Substituting in equation (1) the value of P_{H_2}

$$(1) \quad e = RT \log \frac{(k_2)^{1/2} c}{c} \quad \text{or} \quad e = RT \log \frac{K c_H}{c_{H^+}}$$

which shows that the potential of the cathode is a measure of its reducing power, since it is determined by the concentration of the nascent hydrogen, assuming that c_{H^+} , the concentration of the hydrogen ions, is constant.

Variations of the cathode potential may be obtained in a number of ways. One method of changing the reducing power of a cathode is to vary the current density on it. The increase in potential difference that can be obtained in this way is not very great. This can be shown by the following table, in which are given the current densities

(14) Thompson, M. Applied Electro chemistry p. 69-70
(1911)

and corresponding potentials of cathodes of different metals which refer to the normal hydrogen electrode as zero.⁽¹⁵⁾⁽¹⁶⁾

TABLE I

Cathode Potentials of Metals at Different Current Densities in 2 Normal H_2SO_4

Amperes per Square Cm.	Mercury	Copper	Tin	Nickel
0.01	1.19	0.57	0.97	0.55
0.05	1.26	0.70	1.11	0.67
0.11	1.30	0.77	1.16	0.73
0.15	1.32	0.82	1.18	0.78

It can be seen that the potential difference between electrode and solution does not increase greatly with increasing current density; however, for a given current density this difference varies greatly with the metal used. This variation is due to the overvoltage for the particular metal in question. The reducing power of a cathode can, therefore, be greatly varied by using different metals as cathodes. For substances which reduce with difficulty, metals having high overvoltages should be most applicable.

(15) Thompson, M. Applied Electro chemistry p.70 (1911)

(16) Tafel, J. Zeitschrift fur physikalische chemie
Vol. 50 p. 710 (1905)

Because the conditions of measurement are difficult to standardize, the various values of overvoltages which have been determined for the metals are not at all consistent. The following table will give some idea of the relative values for the different metals. (17)

TABLE II

Overvoltages of Metals at Varying Current Densities

Amp. per sq. cm.	Zn	Cd	Cu	Pb	Hg
0.001	0.718	0.981	0.479	-----	0.92
0.010	0.746	1.134	0.584	1.090	1.03
0.050	0.926	1.211	-----	1.168	1.06
0.100	1.064	1.210	0.801	1.179	1.07
0.200	-----	1.228	0.988	-----	-----
0.300	1.168	-----	-----	1.217	1.10

Other investigators have listed the above metals in the decreasing order of their overvoltages as: Hg, Pb, Zn, Cd, Cu. (18)

(17) International Critical Tables Vol. VI p. 339

(18) Watts, O.P. Lab. Course in Electro chemistry
p. 121 McGraw-Hill (1914)

Another important factor in electrolytic reduction is the catalytic effect of the metal composing the cathode. As a result of this effect, a substance may be more easily reduced on one cathode than another, even though the overvoltage is the same for both cathodes. Thus W. E. Bradt⁽¹⁹⁾ reported Cu as being very effective in the reduction of p-nitrophenetole, giving results as good as Pd or Zn electrodes which have overvoltages considerably above Cu.

Physical structure of the cathode material influences the amount of reduction; roughened cathodes usually giving better results than smooth ones.⁽²⁰⁾

Temperature likewise has its effect. It is obvious that a rise in temperature should increase the rate of reaction between the active hydrogen and the organic depolarizer. Of course there is the opposite effect in regard to overvoltage---a rise in temperature being generally conceded to lower the overvoltage of the particular metal in question.

It is already evident from equation (2), cited earlier,

(19) Bradt, W. E. and Erickson, A. W. Electrochemical Reduction of p-nitrophenetole. Trans. Elec. Chem. Soc. Vol. 75 p. 401 (1939)

(20) Swann, Sherlock Jr. Industrial Possibilities of Electro-organic Reduction, Ind. and Eng. Chem. Vol. 29 p. 1339 - 1341 (Dec. 1937)

that the concentration of the electrolyte will affect the rate of reduction by changing the value of the α_{H^+} term. Indeed, the acidity or alkalinity of the solution will determine the course of the reduction and the point to which it will proceed.

DESIGN OF THE APPARATUS

In carrying out an electrolytic reduction it is of foremost importance to prevent the anodic oxidation both of the starting material and of the reduction product. Accordingly, the use of a divided cell is necessary.

The reduction took place in a 600 ml. tall type beaker (see Figure 1) in which were suspended an anode chamber, the cathode, a glass stirrer, and a thermometer.

The anode chamber consisted of a porous cup (size 5.5 x 12 cm.) which contained the anode and anolyte. Through the anode cup was extended a pyrex tube (1 cm. internal diameter) through which extended a glass stirrer having a propeller blade 2 inches in diameter.

The anode consisted of a cylindrical lead sheet of the same area as the cathode used.

A voltmeter and ammeter were connected (Figure 2) in such a manner that the current or the voltage drop across the cell could be measured. The desired current was regulated by means of a variable resistance connected in series with the cell.

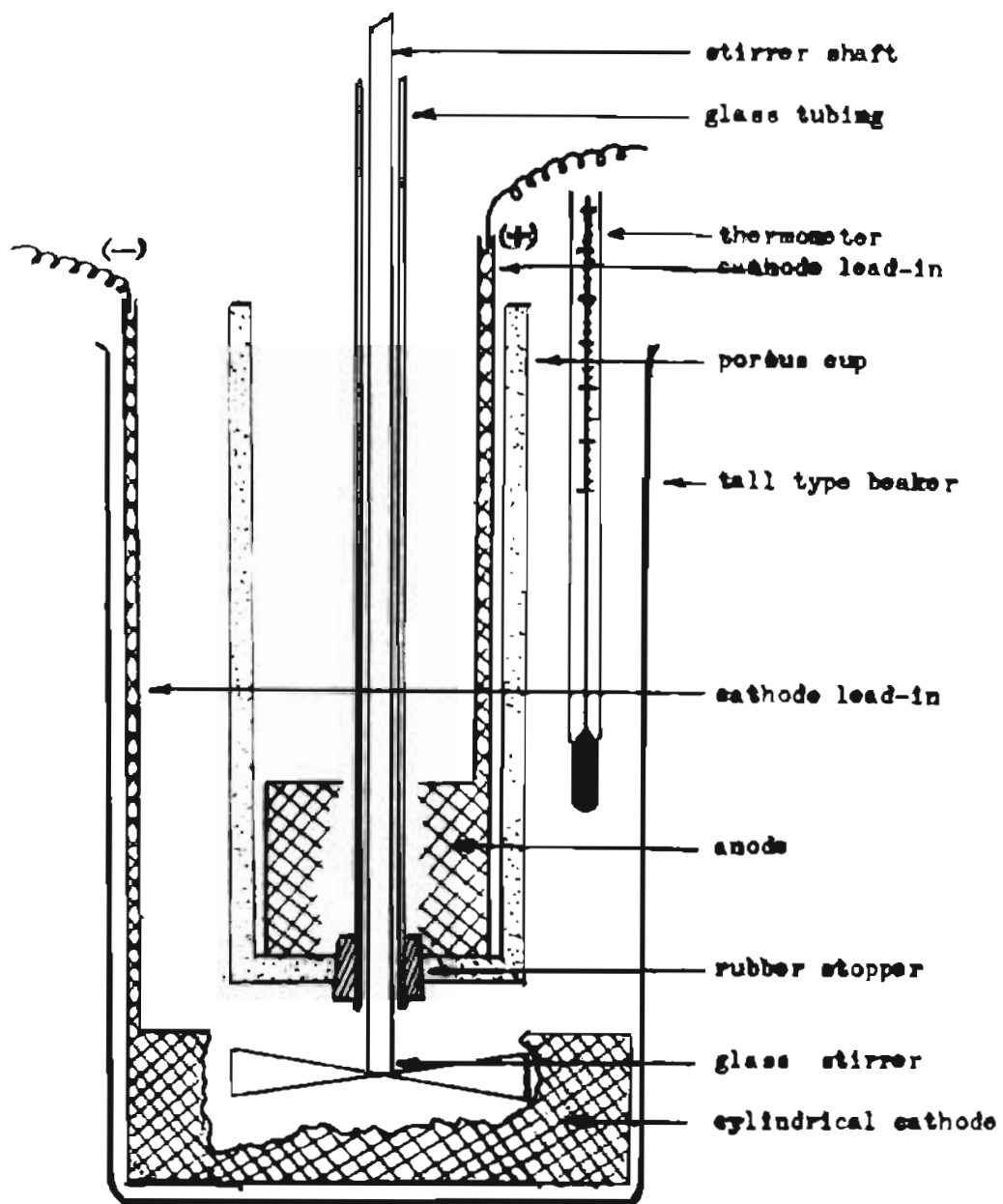


Figure 1 Reduction Cell

This cell was used exactly as drawn for cathodes of lead, zinc, and copper. In all cases, the leads to the cathode were of the same metal as the cathode, and were fused to the cathode proper rather than soldered, to avoid introducing any foreign metals.

Where cadmium was used, the cell was the same, with the exception that stick cathodes were utilized by suspending two of them in the catholyte on opposite sides of the beaker.

A layer of mercury in the bottom of the beaker served as the cathode in the mercury runs. Connection to the cathode was made by means of a glass tube closed at one end and filled with mercury. A platinum wire sealed in the closed end served as the contact.

Before a new porous clay cup was used in any run it was first cleaned by soaking in 10% sodium hydroxide for eight hours, water for eight hours, 10% sulfuric acid for eight hours, water for eight hours, and finally washing with distilled water.

The temperature of the run was controlled by immersing the reduction cell in a tank through which cold water flowed. It was possible by this method to keep the temperature within a five degree range during the course of the run.

The cathode and anode solutions were kept at the same levels. Since electrophoresis accounts for an increase in the volume of the catholyte, water must be added to the

anode solution during the run to keep the levels equal. This increase in volume of catholyte amounted to about 10-15 ml. during an experiment of six hours.

The only direct current source available was a 220 volt line. The following circuits were used in obtaining experimental data.

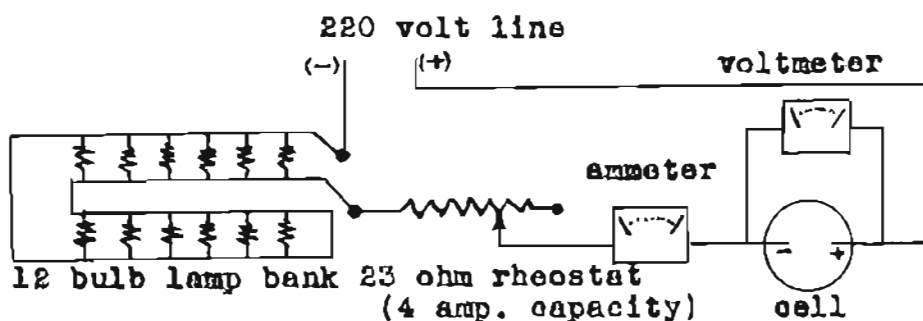


Figure 2 Circuit for Low Current Densities

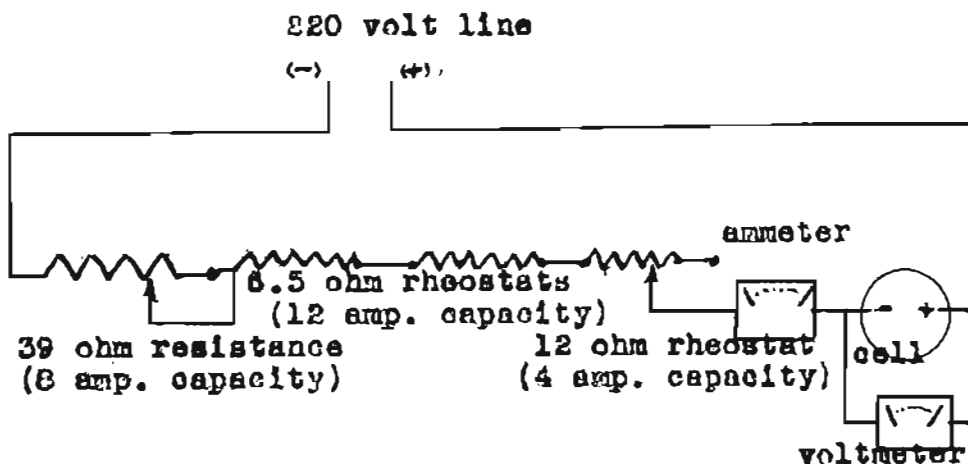


Figure 3 Circuit for High Current Densities

EXPERIMENTAL PROCEDURE

A. Preparation of Pyrrole

The pyrrole used in the following runs was prepared by the dry distillation of ammonium mucate in the presence of glycerin according to Gilman⁽²¹⁾ The fraction distilling over at 128 - 131°C. was taken.

B. Isolation of the Reduction Products

At the conclusion of the run, the anode cup was removed and the outside surface washed well with distilled water; the rinsings being added to the catholyte. Solid KOH was then added slowly in excess to the cathodic solution. To insure against loss of products by volatilization, the temperature during this operation was kept below 30°. The mixture which now had a volume of about 250 ml. was steam distilled until 200 ml. of distillate was obtained. The volume of the residue in the flask was allowed to decrease to about 100 ml. during the distillation to insure getting the concentration of alkali high enough to cause any volatile base to distill over.

The distillate was now made acid to methyl orange with 1-1 HCl. This step converted any pyrroline or pyrrolidine present to hydrochlorides, since they are more basic than pyrrole.

(21) Gilman, H. Organic Syntheses Collective Vol. I
p. 481 Wiley (1932)

On extracting with two 30 ml. portions of ether, any pyrrole not reduced or resinified during the run was removed. The ether extract was dried over KOH and distilled to remove the pyrrole.

The acid water layer from the above extraction process was evaporated to dryness on the steam bath. The remaining brown residue was treated with 25 ml. of 1-1 KOH and steam distilled until 15 ml. of distillate was collected. Solid KOH was added carefully to this distillate to cause any organic base present to separate as an oily layer. The oil was removed by extracting twice with 10 ml. portions of ether and then converted to the hydrochloride salt by shaking with 1-4 HCl. After evaporation on the water bath and recrystallization from an ethanol-ether mixture, the salt was oven-dried at 105° and weighed rapidly.

This method of recovery of the reduction product was used in all the experiments performed in this investigation.

The author believes that it offers a distinct advantage over the methods used by other investigators. It enables one to recover any unchanged pyrrole from the reduction mixture and a pure hydrochloride salt is isolated whose melting point immediately serves to identify the parent reduction product.

C. Identification of the Main Reduction Product
and Preparation of Derivatives

The chief reduction product from all experiments was isolated as the hydrochloride salt. This white deliquescent salt, after recrystallization from an alcohol-ether mixture, gave a melting point of 173-174^oC., which is given in the literature as the melting point of pyrroline hydrochloride⁽²²⁾. It was concluded, because of the sharp melting range, that there was no possibility of the salt being a mixture of pyrroline and pyrrolidine hydrochlorides.

After enough of the hydrochloride had been accumulated, the free base was generated by neutralizing a water solution of the hydrochloride with 1-1 KOH and distilling off the oil which separated. After being dried over K₂CO₃ this oil gave a boiling point of 90-91^o, in agreement with the value for pyrroline⁽²³⁾ given in the literature.

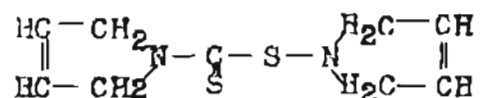
Final and conclusive proof that pyrroline was the substance resulting from the reduction was established by the preparation of the following derivatives which gave the listed melting points:

(22) Hailbron, I. M. Dictionary of Organic Compounds
Vol. III p. 564 Oxford University Press (1938)

(23) Beilstein, F. Handbuch der Organischen Chemie
3rd Edition Vol. IV p. 47-48 (1899)

1. The CS₂ derivative⁽²⁴⁾

0.1 g. of pyrroline in 1.5 ml. of CCl₄ was treated with 0.15 g. of CS₂ in 1.5 ml. of CCl₄. Crystallization of the dithiocarbamate occurs at once in quantitative yield.



The derivative was washed with CCl₄ and alcohol, and recrystallized from ethanol in the form of white leaves that sublime on heating and melted in a closed tube at 201°.

2. The picric acid derivative⁽²⁵⁾

0.1 g. of the hydrochloride salt of pyrroline in 1 ml. of water was treated with a calculated excess of saturated aqueous solution of picric acid and evaporated to dryness. To free the salt of excess picric acid, the crystalline residue was washed with about 3 ml. of cold water and filtered. The easily water-soluble picrate is in the filtrate, while the picric acid does not dissolve. Evaporation and extraction again eliminates the last traces of picric acid. The picrate thus prepared is in the form of yellow prisms and melts at 156°.

(24) Treibs, A. and Dinelli, Dino Liebigs Annalen Vol. 517 p. 170-173 (1935)

(25) Anderlini, F. Berichte Vol. 22 p. 2513-2515 (1899)

3. The chloroplatinic acid derivative(26)

0.1 g. of the hydrochloride salt of pyrroline dissolved in 1 ml. of water was treated with the calculated quantity of 10% aqueous solution of chloroplatinic acid (H_2PtCl_6). The chloroplatinate crystallizes out slowly. The crystals were filtered, washed with 1 ml. of cold water, recrystallized from a small volume of hot water and dried on a porous plate. Orange crystals result; m.p. - 182° with decomposition.

(26) Mulliken, S. P. The Identification of Pure Organic Compounds Vol. II p. 26 Wiley (1916)

PRELIMINARY EXPERIMENTS

A. Reduction of Pyrrole in 2% H₂SO₄ at Low
Current Density

The initial runs were made with the aim of proving or disproving the validity of the results reported in the patent issued to Dennstedt.⁽²⁷⁾ These results were questioned because (1) it is well known that pyrrole is very resistant to reduction; (2) Sakurai reported only a 15% yield of pyrrolidine and no pyrroline from an electrolytic reduction in the presence of a nickel catalyst; (3) the method of isolating the reduction product was vague; (4) no mention was made of the purity of the HCl salt which he isolated; (5) there was no evidence that the reduction product was characterized.

a. Experiment 1 - Electrolysis for 9 Hours

A cylindrical cathode of 100 sq. cm. surface area (both sides) was prepared from commercial lead sheet of 99.9 purity, and etched in dilute nitric acid before use to give it a rough surface. A similar cathode of lead of the same surface area served as the anode. 1-50 sulfuric acid (2% by weight) was used as an electrolyte. The average stirring rate was 750 revolutions per minute.

(27) Dennstedt, op. cit.

Ten cc. of pyrrole was introduced into 200 cc. of the electrolyte and stirred well before any current was passed through the cell. It was observed that the pyrrole dissolved slowly in this concentration of acid, and after 15 minutes was totally dissolved. The electrolysis was carried out at a current density of 0.01 amperes per sq. cm. and a temperature of 23-25°. A fairly vigorous evolution of Hydrogen was noticed during the experiments. The potential drop across the cell mounted slowly from an initial value of 5.2 volts to 5.5 at the end of 9 hours, at which time the run was concluded. The catholyte had not become basic as had been expected, and the odor of pyrrole was evident.

Reduction products were sought by the method described previously. When KOH was added to the solution after the reduction, it was observed that a brownish, sticky oil came to the surface. During the subsequent steam distillation most of this oil was changed to an amorphous, reddish-brown resin which did not distill over. It was concluded that the aforementioned oil was pyrrole which had been partially resinified during the run by the passage of the current and the acid present. Subsequent boiling completed the resinification.

The distillate secured from the first steam distillation was made acid with HCl and extracted with ether. Three and one-half ml. of oil boiling at 128.5-129° was recovered

from this ether extract. A splinter of soft pine soaked in HCl became red at once when held in the vapors rising from a mixture of one drop of this oil and 1 ml. of water. Also 1 drop mixed with 1 drop of HCl (sp. gr. 1.2) reacted vigorously, giving a red-brown resin which became hard on cooling. Further, 1 drop mixed with 1 drop of saturated aqueous isatin solution and 1 drop of dilute H_2SO_4 gave an indigo blue precipitate, soluble in glacial acetic acid and insoluble in ether.⁽²⁸⁾ These observations proved the oil to be unchanged pyrrole recovered from the reduction mixture.

Evaporation of the acid water layer, from which the pyrrole had been extracted, gave a small amount of red-brown residue which yielded no reduction products of pyrrole on further treatment. This brown residue probably resulted from the resinification of pyrrole which was not completely extracted.

(28) Mulliken, S. P. The Identification of Pure Organic Compounds Vol. II p. 228 (1916)

b. Experiment 2 - Electrolysis for 19 Hours

The second run was made under the same conditions as the initial one, except that the time of electrolysis was lengthened to 19 hours. After 11 hours, the voltage across the cell had increased to 5.0, and the cathode solution was basic to litmus. Two hours later, the cathode solution was basic to phenolphthalein - 4 hours later it was basic to thymol blue and the voltage had mounted to 11.0. Sixteen hours after the beginning of the run, the voltage value was 30.0. The temperature now rose to 33°, and a small amount of resinification was apparent in the catholyte. During the next three hours the temperature rose to 40°, making it necessary to conclude the run in order to avoid excessive polymerization (pyrrole polymerizes easily in hot dilute mineral acids). The odor of pyrrole was still noticeable at the end of the reduction.

A 10 ml. aliquot of the cathodic solution was titrated against .0491 N HCl using methyl orange as an indicator. The purpose here was to find approximately how much base was present. Assuming all the basicity was due to pyrroline formed, it was calculated that 2.04 grams of base was present in the total volume of catholyte.

The usual method of recovery yielded 2.3 ml. of unchanged pyrrole and on evaporation of the acidic water layer the familiar red-brown residue was produced. When

1-1 KOH was added slowly to this residue, the odor of ammonia was evident. Steam distillation of this mixture produced 15 ml. of aqueous solution having a peculiar amine-like odor. In the flask was left considerable solid residue of resinous nature.

Upon further treatment, the aqueous distillate gave an oil fuming in moist air, from which was prepared 0.32 grams of hydrochloride salt melting sharply at 174° - the melting point listed for the hydrochloride pyrroline. Further substantiation of this conclusion was realized by preparing the derivatives of chloroplatinic acid and CS_2 . These melted respectively at 183° d. and 201° .

Since the yield of pyrroline did not compare with that calculated from the titration with HCl, it was concluded that a good deal of the basicity of the cathode solution was due to ammonia resulting from the decomposition and resinification of pyrrole during the reduction procedure. Thus no weight can be placed on any value of yield based on titration of the reduction solution.

The results obtained from Experiments 1 and 2 (reduction at .01 amp. per sq. cm.) show that the cathode solution does not become basic until it has been electrolyzed for 11 hours. The patent issued to Dennstedt claimed that it became basic after a few hours.

Continuation of the reduction for 8 hours after the solution had become basic (total time of electrolysis - 19

hours) resulted in a 2.18 percent yield of pyrroline. The patent issued to Dennstedt claimed an almost quantitative yield of pyrroline when the reduction was continued for a few hours after the solution had become basic.

B. Reduction of Pyrrole at Very Low Acid
Concentration and Low Current Density

Since a better yield of pyrroline was obtained in Preliminary Experiment No. 2 than in Preliminary Experiment No. 1, and because pyrrole is soluble in acid and not in a basic solution, it was thought that the reduction was taking place when the catholyte was just barely on the acid side.

Experiment No. 3 was thus carried forward with a view to determining the correctness of this hypothesis. The cathode area, current density, and pyrrole concentration were kept the same. The acid concentration was reduced to 2 ml. in 500 ml. of water (1-1500 by weight). All the pyrrole did not go into solution at this acid strength. The cathode solution reacted basic to litmus after 7-1/2 hours; the voltage increase was slight. During the remainder of the run, dilute H_2SO_4 was added to keep the voltage at 25-30. At this potential the liquor in the cell was just barely acid.

The run was continued for 13 hours; five ml. of unchanged pyrrole was recovered, and .03 grams of the hydrochloride of pyrroline isolated (0.2% yield of pyrroline).

A comparison of the yields obtained in Experiments No. 2 and No. 3 led the investigator to believe that all the reduction in Experiment No. 2 may have occurred after the solution had become basic. To determine the validity of this assumption, the next experiment was carried out in a slightly basic electrolyte.

C. Reduction of Pyrrole in a Basic Electrolyte at Low Current Density

Experiment No. 4 was carried out by starting at a very low acid concentration (2 drops in 500 ml. of water). After 4 hours, the solution tested basic to phenolphthalein and the voltage read 55-60. Acid was added during the remainder of the run to keep this voltage fairly constant. The solution was tested from time to time with Bogen's Universal Indicator, and showed a pH value of 7-8. Temperature was kept between 23-25° throughout the reduction. Five ml. of pyrrole was recovered. No evidence of any reduction product was found. The conclusion was reached that no reduction was possible in basic solution.

A comparison of the results of Experiments 2 and 3 with the results from Experiment 4 shows that the reduction needs to be carried out in a definitely acid solution. Pyrrole was found to be quite soluble in dilute acid solution, very slightly soluble in a neutral solution, and insoluble in basic solution. Since the success of the reduction would depend on an intimate contact of pyrrole with the nascent

hydrogen produced at the cathode, reduction is more probable to occur when the pyrrole is dissolved in the electrolyte than when it is in suspension. The patent issued Dennstedt claimed that the reduction proceeded well in either acid or basic medium.

D. Possibility of Using Other Acids as Electrolytes

Since pyrrole has such a great tendency to resinify in the presence of mineral acids, an investigation of the possibility of using an organic acid as an electrolyte seemed necessary.

Pyrrole was found to be easily soluble in glacial acetic acid and did not resinify until heated very strongly. The conductance of the cell using this electrolyte was, however, found to be too low to make any runs possible.

Sodium acetate-glacial acetic acid solutions dissolved pyrrole easily, but they also gave the cell a resistance too high to make their use possible. Acetic acid-water mixtures were also found to possess a fair solvent power for pyrrole, but here again they could not be used because of their resistance to current flow. Attention was next turned to acetic acid-H₂SO₄ solutions, but this possibility had to be abandoned because these solutions caused pyrrole to resinify more easily than did H₂SO₄-water solutions.

Because of these observations it was decided to use H₂SO₄ as the electrolyte in determining the effect of other variables.

E. Experiments to Determine the Change in Concentration
of Electrolyte During Electrolysis

It is an acknowledged fact that the acid concentration will change during electrolysis if a divided cell is used. The catholyte decreases in acid concentration due to a migration of H_2SO_4 through the porous clay cup into the anolyte, which, in turn, becomes more concentrated.

In order to keep the acid concentration approximately constant during a run, acid will thus have to be added to the catholyte at a known rate to offset the decrease due to migration.

Accordingly, the next runs were made by electrolysis of sulfuric acid solutions alone, at 20-25°, to determine the decrease in acid concentration per unit of time. The same apparatus was used, but current density, cathode area, and acid concentration were varied, and these effects were evaluated. At half-hour intervals during the electrolysis, 5 ml. aliquots were withdrawn from the catholyte and titrated against 0.1 normal sodium carbonate. Differences in successive values gave the corresponding decrease in concentration per 30 minute intervals. To make sure that conditions were normal, the first aliquot was withdrawn 15-30 minutes after the run had started. Total weight of sulfuric acid present in catholyte was calculated as follows:

$$\begin{aligned} (\text{ml. base})(N. \text{ of base})(\text{m.e. wt. of } H_2SO_4) &= \text{wt. } H_2SO_4 \\ \frac{(\text{wt. } H_2SO_4)(\text{vol. cathode solution})}{\text{volume of aliquot}} &= \text{total wt. } H_2SO_4 \end{aligned}$$

The initial volume of catholyte taken was 200 ml., therefore, each aliquot removed decreased this volume by 5 ml. Volume change due to electrophoresis was disregarded, since it amounted to only approximately 10 ml. over a period of six hours.

Experiments 5 and 6 were carried out to determine the rate of change of acid concentration with current density. Two percent H_2SO_4 was electrolyzed at a lead cathode of 100 sq. cm. area and a temperature of 20-25°. In Experiment No. 5 a current density of 0.025 amperes per sq. cm. was used; in Experiment No. 6 a current density of 0.05 amperes per sq. cm.

A comparison of the results from these two experiments (see Table III) shows that doubling the current density also doubles the rate at which the acid concentration of the catholyte decreases.

Experiments 7 and 8 were run at a sulfuric acid concentration of 2% and 4% respectively. The electrolysis was carried out using a lead cathode of 50 sq. cm. area and a current density of 0.1 amperes per sq. cm. The results show that the initial concentration of H_2SO_4 does not effect the migration rate (see Table III).

The ratio of current densities in Experiments 6 and 7 is 1:2, while the ratio of the cathode areas is 2:1. The rate of change of the acid concentration in the catholyte in these two experiments was the same. Since

it was already proved that doubling the current density doubled the rate of change in acid concentration, it was concluded that decreasing the cathode area by one-half changes the rate of migration by the same amount. Thus in Experiments 6 and 7 these two results cancel each other, and the results are identical.

TABLE III
CHANGES IN ACID CONCENTRATION OF THE CATHOLYTE
DURING ELECTROLYSIS

Five ml. samples withdrawn at 30 minute intervals;
Temperature: 20-25°C.; Catholyte solution: 200 ml.
H₂SO₄.

Cathode area (sq. cm.)	Current density (amp/cm. ²)	Initial acid conc.	Time (min)	Total acid present	Loss of acid in catholyte
Experiment No. 5					
100	0.025	2%	0	3.83 g.	
			30	3.12	0.51 g.
			60	2.64	0.48
			90	2.18	0.46
			120	1.72	0.46
			150	1.27	0.45
Experiment No. 6					
100	0.050	2%	0	3.14 g.	
			30	2.12	1.02 g.
			60	1.20	0.92
			90	0.27	0.93
Experiment No. 7					
50	0.10	2%	0	3.86 g.	
			30	2.87	0.99 g.
			60	1.93	0.94
			90	1.03	0.90
			120	0.15	0.88
Experiment No. 8					
50	0.10	4%	0	8.18 g.	
			30	7.07	1.11 g.
			60	6.13	0.94
			90	5.12	1.01
			120	4.18	0.94
			150	3.24	0.94

EXPERIMENTS TO DETERMINE THE EFFECT OF CURRENT DENSITY

Aqueous sulfuric acid solution of concentration 2% by weight was employed as the electrolyte. Ten ml. of pyrrole dissolved in 200 ml. of this solution was electrolyzed for six hours while being stirred at a rate of 750 revolutions per minute. The cathodes were prepared from commercial lead sheet and had a cylindrical form. The temperature of the catholyte was kept between 20-25°C. The acid concentration was held approximately constant during the runs by adding 1-2 H₂SO₄ at a calculated rate by means of a burette. The data for calculating the rate of addition were taken from the preceding experiments on change of acid concentration during electrolysis.

The yields of reduction product were calculated from the amount of hydrochloride salt obtained. Since this salt melted sharply at 174°C. , it was assumed to be the hydrochloride of pyrroline. The picrate and CS₂ derivatives melting at 155° and 201° respectively, definitely established this assumption as true.

A consideration of Table IV and Figure 4 will show that the yield of pyrroline varies with the current density. The highest yield of pyrroline was secured when a current density of 0.1 amperes per sq. cm. was used. The evolution of hydrogen was evident in all these runs, but at a current density

of 0.2 amperes per sq. cm. it was especially vigorous. A reddish-brown resin was obtained in every reduction during the isolation of the products. Due to the fact that 5 amperes was the maximum current that could be run through the circuit, the higher current densities had to be obtained by changing cathode areas.

In order to determine if this change of cathode area has any effect on the reduction, Experiments 10 and 11 were run at the same current density using cathodes 100 sq. cm. and 50 sq. cm. area respectively. Examination of Table IV and contents shows the result to be the same within experimental error. A change in the area of the cathode was therefore concluded to have no effect on the reduction. Cathode area, thus, cannot be considered a variable in these experiments, and all the results shown in Table IV are comparable.

Duplicate runs made at current densities of 0.1 and 0.2 amperes per sq. cm. showed the yields to be capable of repetition.

TABLE IV

EFFECT OF CURRENT DENSITY

Cathode solution: 10 ml. pyrrole + 200 ml. 2% H₂SO₄;
 Anode solution: 2% H₂SO₄; Cathode and anode: lead sheet;
 Time: 6 hours: Temperature: 20-25°C.; Stirring: 750 r.p.m.

Exp. No.	Current density, amp./cm ²	Cathode area	Voltage across cell	Pyrrole recovered	C ₄ H ₇ N.HCl	Yield of C ₄ H ₇ N
		100	5.5-7.0	3.5 ml.	0.41 g.	2.78%
10	0.050	100	6.0-8.0	3.0 ml.	0.50 g.	3.40%
11	0.050	50	6.0-8.0	3.1 ml.	0.52 g.	3.60%
12	0.10	50	10 - 12	2.0 ml.	0.69 g.	4.69%
13	0.10	50	10 - 12	1.5 ml.	0.65 g.	4.41%
14	0.15	33	12 - 14	1.0 ml.	0.37 g.	2.55%
15	0.20	25	16 - 19	3.0 ml.	0.00 g.	0.00%
16	0.20	25	16 - 19	3.0 ml.	0.06 g.	0.41%

EXPERIMENTS TO DETERMINE THE EFFECT
OF ACID CONCENTRATION

An investigation of the effect of variation of the concentration of the sulfuric acid was conducted at the previously determined optimum current density and at the same time and temperature. Acid was added to the cathode solution during the runs to keep the concentration constant. The chemical procedure used was that of the previous experiments.

In addition to the usual identification of the products as the CS_2 and picrate derivatives, a boiling point was also determined and found to be 90-91°C. at 744 mm.

Examination of Table V and Figure 5 shows that an acid concentration of 5% by weight gave the highest material yield of pyrroline. Increasing the concentration beyond this point had a negative effect which was ascribed to increased resinification during the reduction. This conclusion is borne out by the fact that less pyrrole was recovered when the sulfuric acid concentration was increased, and more resin was noted to be present during the recovery of the reduced products.

TABLE V
EFFECT OF ACID CONCENTRATION

Cathode solution: 10 ml. pyrrole + 200 ml. H₂SO₄ (see column 1); Anode solution: H₂SO₄ of same concentration as catholyte; Cathode and anode: commercial lead sheet 50 sq. cm. area; Time: six hours; Temperature: 20-25°C; Stirring: 750 r.p.m.; Current density: 0.1 amp. per cm²

% H ₂ SO ₄ by wt.	E. M. F. across cell	Pyrrole recovered	C ₄ H ₇ N.HCl	Yield of C ₄ H ₇ N
2.0	10 - 12	2.0 ml.	0.69 g.	4.69%
2.0	10 - 12	1.4 ml.	0.65 g.	4.41%
3.5	8 - 9	1.0 ml.	0.63 g.	4.28%
3.5	8 - 9	1.0 ml.	0.69 g.	4.69%
5.0	6.5 - 8	1.0 ml.	1.40 g.	9.50%
5.0	6.5 - 8	1.0 ml.	1.32 g.	9.00%
6.5	6.5 - 7	0.5 ml.	0.76 g.	5.16%
10	5.5 - 6.0	none	0.68 g.	4.62%

EFFECT OF CURRENT DENSITY

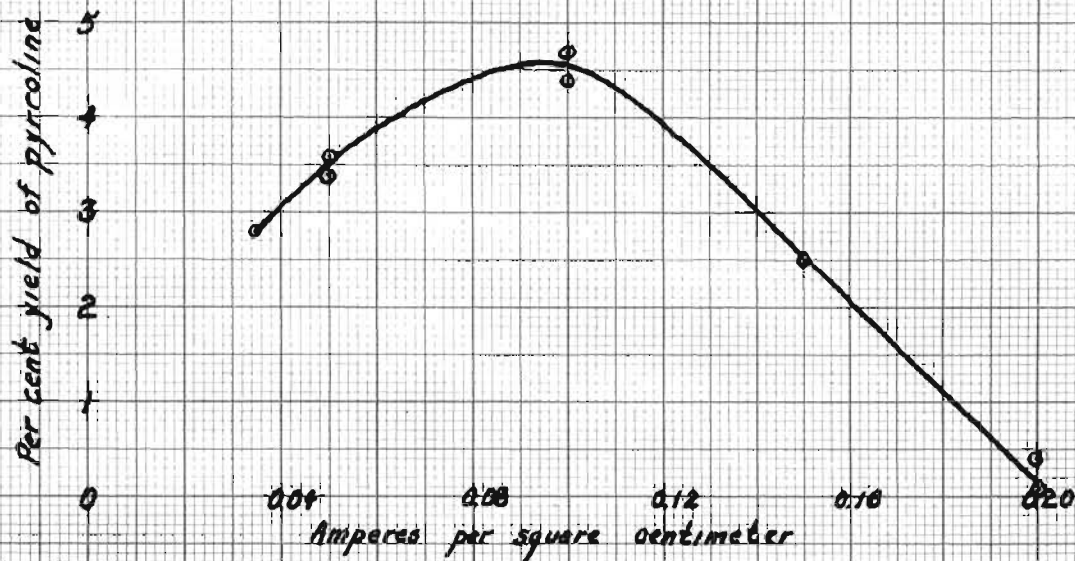


FIGURE 4

EFFECT OF ACID CONCENTRATION

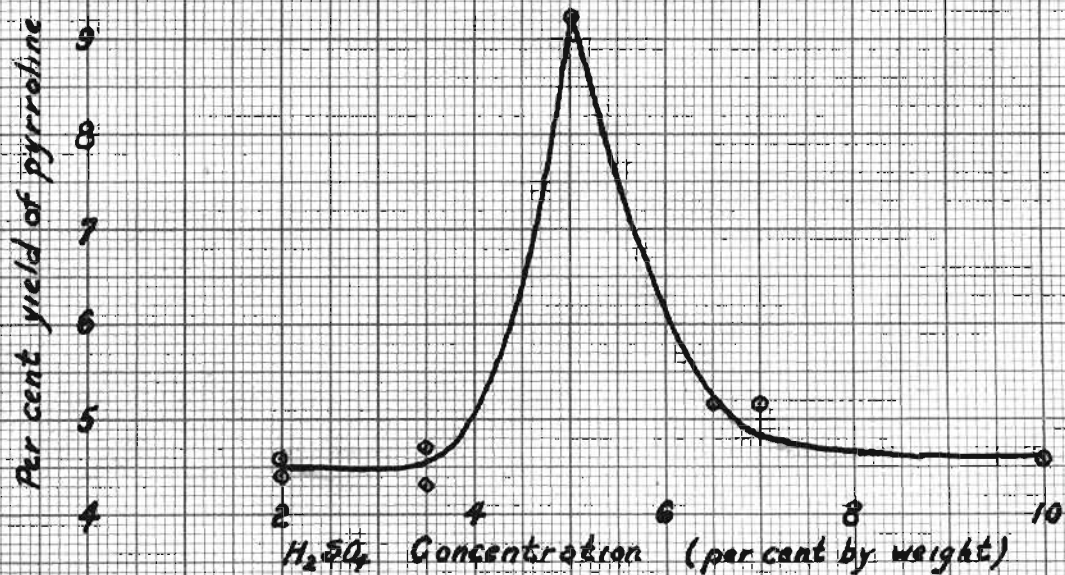


FIGURE 5

EXPERIMENTS TO DETERMINE THE EFFECT OF
TEMPERATURE

Examination of Table VI shows the effect obtained by varying temperature conditions. The low temperature run (4-5°C.) was carried out by placing the reduction vessel in an ice-salt mixture; the length of the run was six hours. Acid concentration was again held constant during the reduction. At the conclusion of the run, the cathode solution was clear and colorless. Addition of solid KOH caused the appearance of some sticky gum and oil which, on later boiling, gave the usual resin.

The high temperature run, made by heating the cell with a water bath arrangement, had to be discontinued after 1 and a half hours had elapsed. A great deal of resin precipitated and formed a heavy foam which the hydrogen forced out of the cell in copious amounts. Treatment of the cathode solution following reduction resulted in more resin being formed.

These results show that a temperature of 20-25° is most suitable. Higher temperatures result in more resinification; lower temperatures decrease the activity of one or the other of the reactants. It is likely that the ability of pyrrole to react with the hydrogen is impaired.

TABLE VI
EFFECT OF TEMPERATURE

Cathode solution: 10 ml. pyrrole + 200 ml. 5% H₂SO₄;
Anode solution: 5% H₂SO₄; Cathode and anode: lead
sheet 50 sq. cm. area; Current density: 0.1 amp. per
sq. cm.; Stirring: 750 r.p.m.

Temp. °C.	Time (hrs.)	E. M. F. across cell	Pyrrole recover- ed	C ₄ H ₇ N.HCl	Yield of C ₄ H ₇ N
4 - 5°	6	8 - 10	3.5 ml.	0.14 g.	0.95%
20-25°	6	6.5- 8	1.0 ml.	1.36 g.	9.25%
45-50°	1.5	8 - 14	0.5 ml.	0.27 g.	1.83%

EXPERIMENTS TO DETERMINE THE EFFECT OF
VARIATION OF TIME

An investigation of the effect of time on the reduction of pyrrole proved very interesting. The experiments were carried on at the previously determined optimum conditions.

It will be seen (Table VII and Figure 6) that the yield of pyrroline increases with time until a maximum is reached at six hours. Further increase in time of the reduction does not increase the material yield. The small decrease in yield of pyrroline after the six hour period can probably be attributed to physical factors such as loss by absorption in the porous cup or by occlusion in the resin formed from pyrrole. Also increased time of reduction was observed to result in an increase of the resinification of pyrrole.

TABLE VII

EFFECT OF VARIATION OF TIME

Cathode solution: 10 ml. pyrrole + 200 ml. 5% H₂SO₄
 Cathode and anode: lead sheet 50 sq. cm. area;
 Current density: 0.1 amp. per sq. cm.; Temperature:
 20 - 25°C.; Stirring 750 r.p.m.

Time (hrs.)	E. M. F. across cell	Pyrrole recovered	C ₄ H ₇ N.HCl	Yield of C ₄ H ₇ N
3	7.5 - 8.5	3.0 ml.	0.79 g.	5.36%
4.5	7.0 - 9.0	1.5 ml.	0.92 g.	6.25%
6	6.5 - 8	1.0 ml.	1.36 g.	9.25%
8	6.5 - 8.5	1.0 ml.	1.29 g.	8.75%
12	8.0 - 9.0	0.5 ml.	1.21 g.	8.22%

EFFECT OF TIME

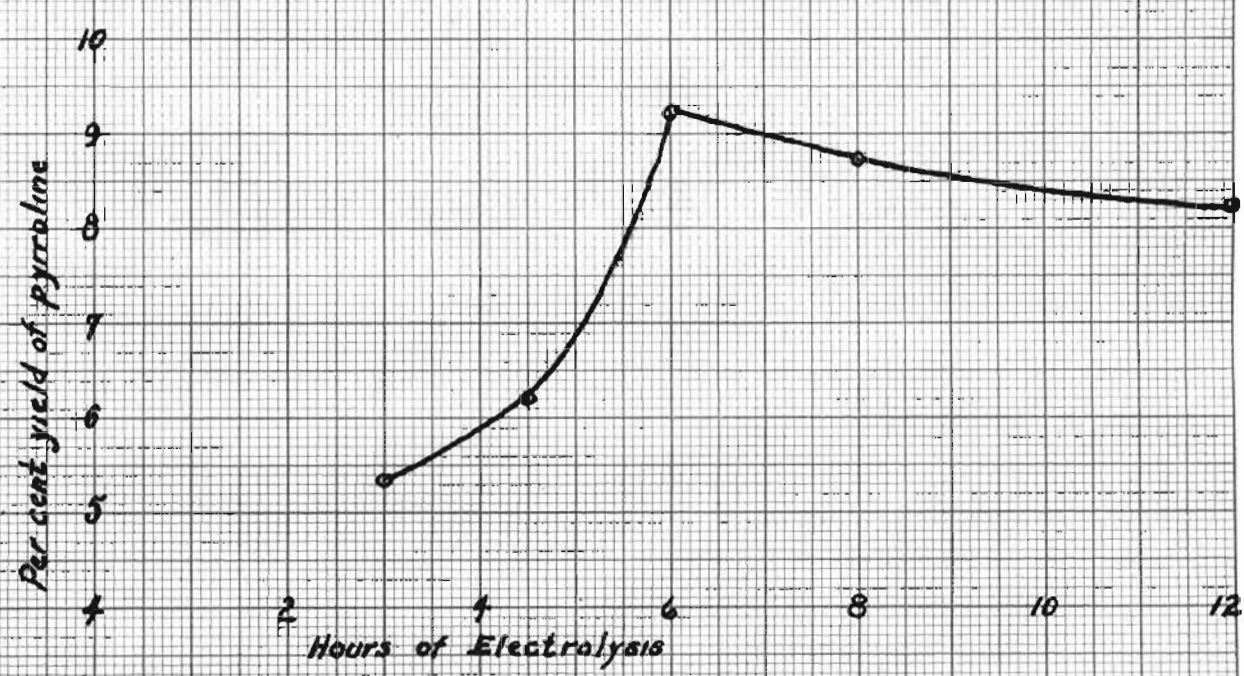


FIGURE 6

EXPERIMENTS TO DETERMINE THE EFFECT OF
PURITY OF PYRROLE

The effect of the purity of pyrrole on its subsequent reduction seemed worthy of investigation, since there have been cases in which electrolytic reduction has failed because of the presence of small amounts of impurities.

Accordingly, a very pure pyrrole was prepared from the pyrrole boiling at 128-131° by means of the potassium salt⁽²⁹⁾ Pyrrole with an excess of five times the calculated quantity of coarsely powdered KOH was heated in a flask with a reflux condenser at a temperature of 80-100° for 18 hours and finally under the full flame of a bunsen burner for 1 hour. The reflux condenser was then replaced by a horizontal condenser and all volatile matter was distilled off. The melted mass was allowed to cool and water was added. Due to hydrolysis of the potassium salt, a pleasant smelling oil separated out. This oil was separated by distillation, dried over NaOH, and again distilled. A boiling range of 128-129° was observed.

The pyrrole thus prepared was dissolved in 200 ml. of 2% sulfuric acid and subjected to the regular electrolytic reduction procedure at a Pb cathode of 100 sq. cm. and a current density of 0.01 amperes per sq. cm. for

(29) Anderson, L. Liebigs Annalen Vol. 105 p. 352
(1858)

nine hours. Treatment of the cathodic solution in the usual way showed that no reduction had taken place. The experimental evidence was in agreement with that obtained from Preliminary Experiment No. 1 (see page 27).

Another reduction using this purified pyrrole was made at a Pb cathode 50 sq. cm. in area, at a current density of 0.1 amperes per sq. cm., using 5% sulfuric acid as the electrolyte. Time of electrolysis was six hours. This run yielded 1.28 grams of pyrrolino hydrochloride; on the basis of pyrrolino, a percentage yield of 8.70%.

This investigation showed that the results obtained by using pyrrole with a boiling range of 128-131° are reliable because they are in agreement with those obtained when a purified is used.

EXPERIMENTS TO DETERMINE THE EFFECT OF ELECTRODE MATERIAL

A study of the effect of different cathode metals was conducted at the previously determined optimum current density, acid concentration and temperature. The metals chosen, with the exception of copper, were those possessing high overvoltages (see Table II, page 10).

Mercury used as cathode material was purified sufficiently by being allowed to fall in a fine spray through a quantity of 10% KOH solution and then through 15% nitric acid. A 3-foot length of 1-inch glass tubing fused at the bottom to a small U-type exit tube was used to contain the acid and base solutions. To produce the spray, the stem of a glass funnel was drawn down so as to leave only a capillary opening through which the mercury flowed. After being passed through the base and acid solutions a number of times, the mercury was allowed to fall through distilled water to remove any salts formed.

Cadmium electrodes were made from stick cadmium of the following maximum limit of impurity: arsenic, 0.000%; copper, 0.000%; iron, 0.005%; lead, 0.01%; zinc, 0.08%.

A copper cathode was cut from pure Cu sheet that had been well sandpapered and then etched in nitric acid.

A zinc electrode was made from a well cleaned zinc sheet and was etched with nitric acid to give it a rough surface.

A consideration of Table VIII reveals that the best yields of pyrroline are obtained with zinc and lead cathodes; Cd and Hg give yields somewhat lower; Cu (of much lower overvoltage) gave no pyrroline at all. The expected correlation between overvoltages and material yield is very evident when the yields from Pb and Zn are compared to Cu. The difference between results with Zn and Pb cathodes and those obtained with Cd are more difficult to explain. However, it is well to remember that the values of these overvoltages are highly questionable, and some investigators do list Pb and Zn above Cd in the series. (30)

Mercury, which is generally considered to have an overvoltage comparable to Pb and Zn gave surprisingly low yields of pyrroline. A check run was made in this instance. Possibly the effect noted was due to physical nature of the surface since all solid metal cathodes used were etched before use.

(30) Watts, O.P. Laboratory Course in Electrochemistry
p. 121 (1914) McGraw Hill Book Company

TABLE VIII
EFFECT OF CATHODE MATERIAL

Cathode solution: 10 ml. pyrrole + 200ml. 5% H_2SO_4 ;
Anode solution: 5% H_2SO_4 ; Anode: lead sheet 50 sq. cm.
area; Cathode area: 50 sq. cm.; Current density: 0.1
amp. per sq. cm.; Temperature: 20-25°C.; Time: 6 hrs.
Stirring: 750 r.p.m.

Metal	E. M. F. across cell	Pyrrole recovered	$C_4H_7N.HCl$	Yield of C_4H_7N
Lead	6.5 - 8	1.0 ml.	1.36 g.	9.25%
Zinc	6.5 - 7.5	0.5 ml.	1.10 g.	7.48%
Cadmium	6.0 - 7.0	1.2 ml.	0.92 g.	6.25%
Mercury	8.0 - 9.0	1.2 ml.	0.63 g.	4.41%
Mercury	8.0 - 9.0	1.2 ml.	0.71 g.	4.02%
Copper	6.0 - 7.0	2.0 ml.	none	none

EXPERIMENTS TO DETERMINE THE EFFECT OF
PYRROLE CONCENTRATION

Since the concentration of the organic depolarizer might have some effect on the yield of pyrroline, a reduction was made with the concentration of pyrrole double that used in former runs.

In this experiment the catholyte contained 20 ml. of pyrrole in 200 ml. of 5% sulfuric acid. When this amount of pyrrole was used, a portion of it remained undissolved. The reduction run was made at the previously determined conditions for optimum yield.

The results show (Table IX) no increase in the yield of pyrroline. Instead there was a slight decrease in the amount of reduction product obtained. Much more resin was present during the recovery procedure. This undue amount of resin may have occluded a good deal of pyrroline which could not be freed by steam distillation. The low yield might thus be accounted for.

In this series of experiments is also included a reduction run in which the pyrrole was added to the electrolyte continuously at the rate of 2 ml. per hour. The initial concentration of pyrrole was 1 ml. in 200 ml. of 5% sulfuric acid. The pyrrole was added under the surface of the catholyte by means of a burette with a capillary stem. After 10 ml. of pyrrole had been added (4-1 2 hours), the run was continued 1-1 2 hours more. During the run there

was evidence that because of entrainment in escaping bubbles of hydrogen, some pyrrole was lost before it dissolved in the electrolyte.

An inspection of Table IX shows that the yield of pyrrolone was only .75% less than obtained by the regular method, and more unchanged pyrrole was recovered. The method may offer a slight advantage.

TABLE IX
EFFECT OF PYRROLE CONCENTRATION

Cathode solution: pyrrole + 5% H₂SO₄; Cathode and anode: lead sheet 50 sq. cm. area; Temperature: 20-25°C; Time: 6 hrs.; Current density: 0.1 amp. per sq. cm.; Stirring: 750 r.p.m.

Pyrrole concentration	E. M. F. across cell	Pyrrole recovered	C ₄ H ₇ N.HCl	Yield of C ₄ H ₇ N
10 ml. + 200 ml. acid	6.5-8.0	1.0 ml.	1.36 g.	9.25%
20 ml. + 200 ml. acid	7.0-8.0	1.7 ml.	1.03 g.	7.00%
1 ml. + 200 ml. initially; 9 ml. added	6.0-8.0	1.7 ml.	1.25 g.	8.50%

SUMMARY

The electrolytic reduction of pyrrole has been studied at various cathodes; the effect of current density, time, temperature; acid concentration of the electrolyte, concentration of the depolarizer, and purity of the starting product have been investigated.

The reduction product was characterized as a 2-5 dihydrogenated pyrrole (pyrroline). In addition, a resin was formed during the electrolysis.

The highest yield (9.25%) was obtained by electrolyzing a solution of pyrrole in 5% H_2SO_4 for six hours at a lead cathode using a current density of .1 ampere per sq. cm.

A zinc cathode was found to give almost the same yields of pyrroline as lead. Cadmium and mercury cathodes gave lower yields. No reduction occurred when a copper cathode was used.

The great tendency of pyrrole to resinify in dilute mineral acid was found to prevent the use of higher temperatures in the reduction. Temperatures below $20-25^{\circ}$ resulted in decreased yields of pyrroline.

The reduction was proved to take place only in an acid solution.

The quantitative reduction of pyrrole at very low current densities claimed, in a patent issued to Dennstedt, could not be duplicated.

The yield of the reduction product could not be increased above a certain limit by increasing the time of electrolysis.

The yield of reduction product increased with an increase in acid concentration up to 5% H_2SO_4 . Further increase resulted in a smaller yield due to increased resinification.

The yield varied with current density until a maximum was reached at .1 amperes per sq. cm. Further increase resulted in smaller yields and more resin.

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