

T
153

THE POLAROGRAPHIC

REDUCTION

OF

N-NITROSO AMINES

BY

MARY O. TASHDJIAN

submitted in partial fulfillment for the requirements
of the degree Master of Science
in the Chemistry Department of the
American University of Beirut
Beirut, Lebanon
June, 1955

N-NITROSO AMINES

MARY O. TASHDJIAN

ACKNOWLEDGMENT

I wish to thank Dr. Robert H. Linnell and Dr. R. Bruce Martin for suggesting the subject of this thesis and supervising it with encouragement.

I express my gratitude to the Research Corporation of New York City for the financial support of this project.

ABSTRACT

The Polarographic reduction of three N-Nitroso-Compounds is studied at the dropping mercury electrode. The process is found to be irreversible, the rate determining step has been elucidated and a mechanism postulated.

TABLE OF CONTENTS

	<u>Page</u>
Introduction	1
Experimental Procedure	11
Results	18
Discussion	23
Tables	30
Figures	36
Bibliography	43

LIST OF TABLES

	<u>Page</u>
Table 1.- Concentration Range.....	30
Table 2.- N-Nitroso-dimethylamine.....	31
Table 3.- N-Nitroso-piperidine.....	32
Table 4.- N-Nitroso-diphenylamine.....	33
Table 5.- N-Nitroso compounds in 50% ethyl alcohol.....	34
Table 6.- Temperature experiment.....	35

LIST OF FIGURES

	<u>Page</u>
Fig. 1.- Current vs. Voltage for N-Nitroso-piperidine.....	36
Fig. 2.- $i_d(\text{ua}/2.85)$ vs. $C(\text{moles/liter})$ for N-Nitroso-dimethylamine.....	37
Fig. 3.- $i_d(\text{ua}/2.85)$ vs. $C(\text{moles/liter})$ for N-Nitroso-piperidine.....	38
Fig. 4.- $E_{1/2}$ vs. pH for N-Nitroso- dimethylamine (A).....	39
for N-Nitroso-piperidine (B).....	39
Fig. 5.- $E_{1/2}$ (volts) vs. pH for N-Nitroso-diphenylamine.....	40
Fig. 6.- $i_d(\text{ua})$ vs. Temperature $^{\circ}\text{C}$ for N-Nitroso-piperidine.....	41
Fig. 7.- $E_{d.e.}$ (volts) vs. $\log(i_d - i)/i$ for N-Nitroso-dimethylamine.....	42

INTRODUCTION

Polarography is an electrolytic method of analysis. The potential is measured when electrolysis is carried out at the electrodes. One of the electrodes is large and non-polarizable; the other small and polarizable. The electrolysis is carried out at the surface of the polarizable electrode-microelectrode.

Definition of terms used:-

Polarogram:- It is the S-shaped curve obtained by the plot of current versus applied voltage, during the electrolysis at the microelectrode. A typical polarogram is shown in Fig. 1.

Wave-Height:- It is the height of this curve, and is a function of the concentration of the reacting material among other things. See Ilkovic's equation below.

Half-Wave Potential:- It is the potential corresponding to the inflectional point of the curve. This potential is characteristic of the reacting material.

Limiting Current:- When complete concentration polarization occurs at the microelectrode, the current is controlled by the rate of supply of the reacting material to the surface of the drop, and is called limiting current.

There are six types of current which control this rate; adsorption, migration, diffusion, kinetic and catalytic currents.

Adsorption and catalytic currents do not appear in the reduction of nitroso compounds and will not be discussed here.

Migration Current:- It results from the migration of charged particles in the electric field. It is eliminated by adding a large excess of an indifferent electrolyte. "An indifferent salt is one that conducts current but does not react with the substance under investigation nor at the electrode in the range of potential that is studied".⁽¹⁾ An indifferent electrolyte is often called a "supporting electrolyte".

After the elimination of migration current the limiting current becomes a function of either diffusion or kinetic current, and sometimes a combination of both.

Ilkovic has derived the following equation for diffusion controlled processes:-

$$I_d = 605 n D^{\frac{1}{2}} C m^{\frac{2}{3}} t^{1/6}$$

" I_d " is the mean diffusion current (in μa), "m" the weight (in mg) of mercury flowing from the capillary per second, "t" the time necessary for the formation of one drop of mercury, "C" the millimoles of reacting material per liter, "D" the diffusion coefficient of the reducible

1. Muller, H. Otto, The Polarographic Method of Analysis, (Pa. 1951) p.62.

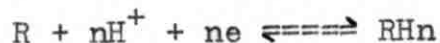
substance (in $\text{Cm}^2 \text{sec}^{-1}$) and "n" the number of electrons involved in the reduction of one molecule of the substance". (2)

Kinetic Current:- There are cases in polarographic reductions where the limiting current is controlled by diffusion of the reacting material and the rate of formation of additional reacting material at the surface of the drop. The current due to the second process is called kinetic current.

In addition to the mentioned currents there is the residual current which appears before reduction of the reacting material. This current is non-faradaic. There is no sign of a wave and the rise of current is almost proportional to the applied potential. The residual current is subtracted from the total current by the tangent method.

Organic Polarography

Hydrogen ions take part in the reduction or oxidation reactions of organic compounds. For an uncharged molecule, a general equation is given



For such an equilibrated system, the potential of the dropping mercury electrode at 25°C is given by

$$E_{d.e.} = E_0 - 0.0591/n \log C^{\circ}RHn/C^{\circ}R(C^{\circ}H^+)^n$$

C° means the concentration at the surface of the mercury drop. If the solution is buffered efficiently then $(C^{\circ}H^+)^n$ in the denominator remains constant and is equal to the hydrogen ion concentration in the body of the solution. The potential of the electrode for a buffered solution is given as

$$E_{d.e.} = E_0 - 0.0591/n \log C^{\circ}RHn/C^{\circ}R - 0.0591/n \text{ pH}$$

The half-wave potential is given as

$$E_{\frac{1}{2}} = E_0 - 0.0591/n \log K_R/K_{RHn} - 0.0591/n \text{ pH}$$

K_R/K_{RHn} is proportional to $(D_R/D_{RHn})^{\frac{1}{2}}$ where D_R is the diffusion coefficient of the reacting material. In most cases $(D_R/D_{RHn})^{\frac{1}{2}}$ is almost one, and the equation for the half-wave potential is given as

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

The potential of the dropping mercury electrode could also be given in terms of $E_{\frac{1}{2}}$

$$E_{d.e.} = E_{\frac{1}{2}} - 0.0591/n \log C^{\circ}RHn/C^{\circ}R$$

If i is the current at any point of the curve, and i_d is the diffusion current in cathodic reduction, then

$$i = K_R C^{\circ}R \qquad i_d - i = K_{RHn}$$

and the above equation could be written as follows

$$E_{d.e.} = E_{\frac{1}{2}} - 0.0591/n \log (i_d - i)/i$$

This equation applies to electrode reductions for which diffusion is the slowest process. The reduction in this case is called "reversible".

If there is a single step in the process which is irreversible, then the reduction mechanism as a whole is irreversible. Irreversible reductions are of several types and in some cases are not well understood.

J. Page⁽³⁾ gives two of these types:

1.- There are reductions in which electron addition is reversible, but the product at the electrode is not stable and further reactions consume it.

2.- The electron addition is irreversible. Hydrogen ions are reduced to atomic hydrogen, which later reacts irreversibly with the organic molecule.

In the first case the plot of current versus voltage is an S-shaped curve. $E_{\frac{1}{2}}$ varies linearly with pH. The plot of $E_{d.e.}$ versus $\log(i_d - i)/i$ gives a straight line, the slope of which determines $n\alpha$; $n\alpha$ being less than one.

$$E_{d.e.} = E_{\frac{1}{2}} - 0.0591/n\alpha \log(i_d - i)/i$$

Polarography in Non-Aqueous Media:-

There are compounds which are not soluble in water, and require organic solvents for solution. The solvent for this purpose should be polar enough to conduct electricity. Ethanol, ethanol-water solvents are often used. The polarographic characteristics in these cases are nearly

3. Page, E.J., Quarterly Reviews, v. 6,
(1952) p. 281.

those of aqueous solutions, but the diffusion current is smaller. There are two reasons for this:-

1.- The great viscosity of non-aqueous solvent, which decreases the diffusion coefficient.

2.- Other factors, such as changes in the nature of the reducible molecule.

Nitroso Compounds

The nitroso group is the $-N=O$ group. The nitrogen could either be attached to a carbon atom or another nitrogen atom. In the second case the compound is called N-nitroso.

There has been very little studies on the polarographic reduction of the N-nitroso group. More is known about simple nitroso compounds of all the facts known so far, the behaviour of the nitroso group is closely related to that of the NO_2 group. The former is shown to be an intermediate of the reduction product of the NO_2 group. (4)

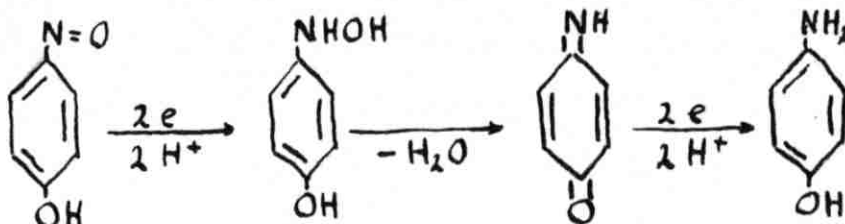
The reduction of the nitroso compound is easier than that of the corresponding nitro compound. The difference is estimated to be about 0.4 volts. (5)

4. Kolthoff, M.I. and Lingane, J.J., Polarography, (New York 1952) p. 746.

5. Gardner, J.H. and Lyons, E.L., Reviews of pure and Applied Chemistry, (1953) p. 164.

The Study of Simple Nitroso Compounds:-

p-Nitrosophenol:- There are four electrons involved in the reduction of this compound. It is reduced to p-amino-phenol

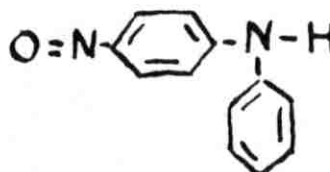


α -Nitroso β -Naphthol:- The behaviour is similar to that of p-Nitrosophenol.

Nitrosobenzene and p-Nitrosodiphenylamine:- Two waves appear. The first one involves two electrons. The second wave of nitrosobenzene is similar to that of phenylhydroxylamine.



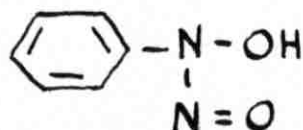
Nitrosobenzene



p-Nitrosodiphenyl-amine

The Study of N-Nitroso Compounds:-

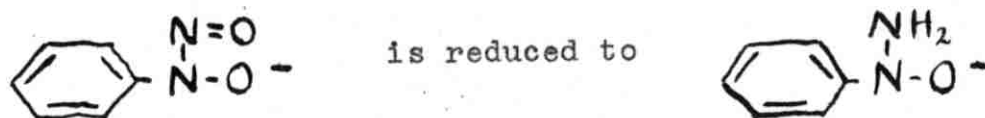
N-Nitrosophenylhydroxylamine⁽⁶⁾:-



6. Kolthoff, M.I. and Lingane, J.J., op.cit.
p. 765.

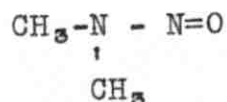
The ammonium salt of this compound is studied at different pH values. In acid medium (pH 1) only one wave is observed, corresponding to six electron reduction to phenylhydrazine.- $C_6H_5-\overset{H}{N}-NH_2$.

Between pH 7 - 9 two waves are observed. The first is pH dependent, while the second is not. In the alkaline medium, the reduction involves four electrons. The dissociation anion



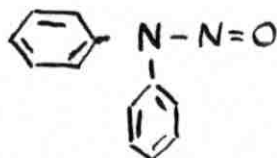
This thesis treats with the polarographic behaviour of three different N-Nitroso compounds:-

1.- Aliphatic



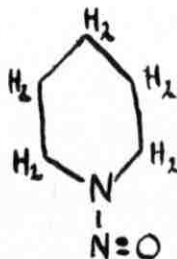
N-Nitroso-dimethyl-amine

2.- Aromatic



N-Nitroso-diphenyl-amine

3.- Heterocyclic



N-Nitroso-piperidine

The purpose of the study is to determine the mechanism of the reduction. The effect of different substituents on nitrogen has been a help in this study. The field is open to more extensive study.

Since nitroso compounds are closely related to nitro compounds, the polarographic behaviour of aliphatic and aromatic nitro compounds will be discussed.

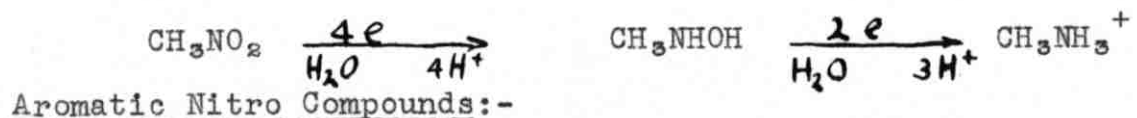
Nitro Compounds

Aliphatic Nitro Compounds:-

The nitro compounds studied are:-

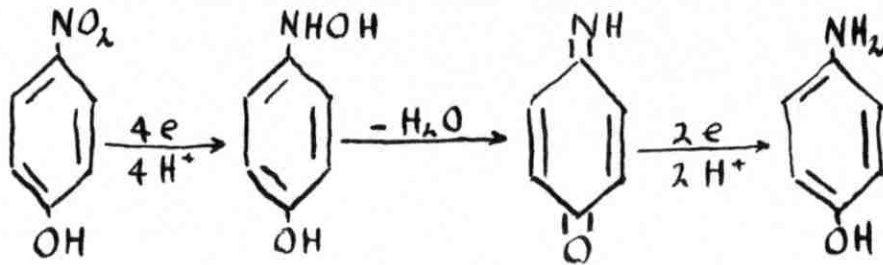
Nitromethane (CH_3NO_2), Nitroethane ($\text{CH}_3\text{-CH}_2\text{NO}_2$), 1-Nitropropane ($\text{CH}_3\text{-CH}_2\text{-CH}_2\text{NO}_2$), 1-Nitrobutane ($\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{NO}_2$).

All of them have one wave in acid medium. Above pH 4.5 a second wave is observed. The first wave involves four electron reduction of the nitro compound to hydroxylamine. The second wave is the reduction of hydroxylammonium ion to alkylammonium ion. Both processes are irreversible.

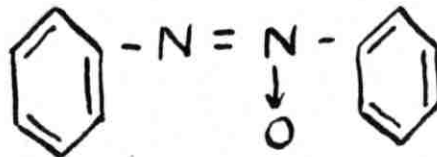


The reduction is with four electrons to phenylhydroxylamine.

In case of o,p, nitrophenol, p-nitroaniline and p-dinitrobenzene, the product phenylhydroxylamine is converted to quinoid forms which can be reduced.



Phenylhydroxylamine:- In acid medium below pH 2 it is reduced by two electrons to aniline. The half-wave potential corresponds to that of the second wave of nitrobenzene. Between pH 2 - 6 the wave is not well defined. At high pH values the compound is converted to azoxybenzene.



Azoxybenzene

EXPERIMENTAL PROCEDURE

A Sargent Model XXII Polarograph was used with a Heyrovsky type cell.

Hydrogen from a Kipp generator was used to remove oxygen from the test solution. It was cleaned as follows: after generation by the reaction of mossy Zn with chemically pure HCl, it was passed through two bottles, containing 30% KOH and the test solution respectively. All rubber tubes were soaked in concentrated KOH, rinsed with distilled water and dried.

Temperature was controlled to $\pm 0.01^{\circ}\text{C}$ by Princo "Magnaset" Thermoregulator.

The cell resistance was measured with an alternating current Wheatstone Bridge.

All pH measurements were taken with a Cambridge portable glass electrode pH meter. In the case of the alcoholic solutions no correction for the change in activity coefficient was made.

The height of mercury was kept constant at 67 cm. The drop time (t) and the weight (m) in mg of each drop, were measured at an applied potential of one volt. These values for m and t were used in all measurements for the determination of the number of electrons from the Ilkovic equation,

$$I_d = 605 nD^{\frac{1}{2}} \text{Cm}^2/\text{s} t^{1/2}$$

Preparation of N-Nitroso Compounds

Nitroso compounds are generally prepared by the reaction of secondary amines with nitrous acid.



Preparation of N-Nitroso-dimethylamine⁽⁷⁾ :-

"A solution of 180 g of sodium nitrite in 200 cc. of warm water is added slowly to 200 g of dimethylamine dissolved in 100 cc. of water acidified with sulfuric acid. When all the nitrite has been added the solution is distilled to dryness. The distillate is acidified and distilled again to remove traces of unchanged amine. The addition of solid sodium carbonate to the distillate causes the nitrosoamine to separate as a pale yellow oil. This is removed and dried in contact with solid potassium carbonate".

The dried nitrosoamine was distilled twice and the physical constants determined. Experimental values were found to be, B.P. 153°C and n_{18}^D 1.4373. Literature values are, B.P. 152 - 153°C and n_{18}^D 1.4374⁽⁸⁾.

-
7. Hickinbottom, J.W., Reaction of Organic Compounds, (London 1945) p. 286.
 8. Charles, D.C. Handbook of Chemistry and Physics, (Cleveland, Ohio 1946) p. 778.
-

Preparation of N-Nitroso-piperidine⁽⁹⁾ :-

A similar procedure was used. Experimental value:
B.P. 215 - 217°C, n_{18}^D 1.4932. Reported values: B.P.
215 - 217°C, n_{18}^D 1.4933⁽¹⁰⁾.

Preparation of N-Nitroso-diphenylamine⁽¹¹⁾ :-

"A solution of 50 g of diphenylamine in 250 g of alcohol is cooled to 0° and 35 - 40 cc. of concentrated hydrochloric acid all at once. Before the hydrochloride of diphenylamine can separate, a solution of 25 g of sodium nitrite in 35 cc. of water is added rapidly and the mixture stirred. The precipitated nitrosoamine is collected by filtration and purified by crystallization from hot light petroleum (b.p. 80 - 100°). It is obtained as massive pale yellow crystals".

M.P. found.- 66 - 67°C, reported.- 66.5°C⁽¹²⁾.

Preparation of Ethyl Alcohol from Solvent :-

Commercial ethyl alcohol was treated with MnO₂ and distilled. The middle fraction of the distillate was used to make a blank test.

The blank test solution contained 50% by volume of ethyl alcohol and 0.1N KCl as supporting electrolyte. Hydrogen was passed through the solution for fifteen

-
9. Hickinbottom, J.W., op.cit.
 10. Beilsteins Handbush Der Organischen Chemie, (4th ed.), v. 20 (1935), p. 83.
 11. Hickinbottom, J.W., op.cit.
 12. Charles, D.C., op.cit. p. 780.
-

minutes. This was thought to be the optimum time for oxygen removal, with the least change in concentration due to evaporation.

The polarogram of the degassed solution has the two waves of oxygen. The wave-heights of these curves were small, and their half-wave potentials did not interfere with those of the nitroso compounds, within the pH range studied.

The middle fraction of the MnO_2 distilled alcohol was used as a non-aqueous solvent.

Preparation of Buffer Solutions:-

The buffers used were the following:-

- 1.- Walpole: 10 cc. 1N sodium acetate, x cc. 1N HCl diluted to 50 cc.
- 2.- McIlvaine: 10 cc. mixture of x cc. 0.1M citric acid and y cc. 0.2M Na_2HPO_4 .
- 3.- Walpole: 10 cc. mixture of x cc. 0.2N acetic acid, and y cc. of 0.2N sodium acetate.

All the values were checked with the pH meter.

Preparation of Supporting Electrolyte:-

A stock solution of 1N KCl was prepared. Dilutions were made so that all test solutions were 0.1N in KCl.

Preparation of Test Solutions:-

N-Nitroso-diphenylamine is soluble in ethyl alcohol but not in water. N-Nitroso-dimethylamine and -piperidine are soluble in water.

Stock solutions of the N-Nitroso compounds were made. Diluting was done with pipettes. The diluting of alcoholic solutions was adjusted to contain 50% (by volume) ethyl alcohol.

Each sample of test solution contained diluted N-Nitroso compound, 0.1N KCl and the proper volume ratio of buffer.

Measurements of Diffusion Current (I_d)

Half-wave Potential ($E_{\frac{1}{2}}$) and $n\alpha$

All the curves were recorded on photographic paper and later traced on transparent graph paper. All measurements were made by counting the squares of the graph paper, except in the case of diffusion current and half-wave potential of N-Nitroso-dimethylamine, where the measurements were done directly on the photographic paper.

A.- I_d and $E_{\frac{1}{2}}$ Measurements:-

1.- Aqueous Solutions:- In the case of the aqueous solutions the polarograms were well defined and the tangent method⁽¹³⁾ was used to determine $E_{\frac{1}{2}}$ and i_d .

2.- Alcoholic Solutions:- The rate of hydrogen bubbling was standardized so that the change in concentration by evaporation of the alcohol could be constant.

13. Willard, H.H., Merritt, L.L. Dean, A.J., Instrumental Methods of Analysis, (New York 1952), p. 292.

At high pH values the polarograms were not well defined. The plateau was not horizontal, but had a slight positive slope and was immediately followed by the reduction wave of hydrogen. The inflectional point between the rising part of the N-Nitroso curve and the hydrogen curve was substituted for the end point of the missing plateau.

The diffusion current was measured in cm by counting squares between the tangents at the half-wave potential, multiplied by the shunt setting, and was changed to microamperes by the galvanometer factor $0.0057/\mu\text{a}/\text{mm}$.

The half-wave potential was measured in cm by counting squares from the vertical zero axis to the inflection point of the curve. This distance, x cm, was changed to volts,

$$E_{\frac{1}{2}} = x/21.6 \text{ (applied potential)}$$

21.6 is the distance in cm proportional to the total applied potential.

The measured potential in volts was standardized against an external saturated calomel electrode, by means of Leeds and Northrup Student Potentiometer. The half-wave potential for the alcoholic solutions was not corrected for the change in liquid junction potential.

B.- Measurements of $n\alpha$:-

At different potentials on the rising part of the curve the current i was measured as follows: a vertical line "y" was drawn from the tangent to the curve, to meet

the rising part of the curve "x". The distance from "x" to the tangent was counted in cm., as squares and was proportional to $i(\mu a)$. Then i_d known $i_d - i$ (cm) was calculated.

The horizontal distance from the vertical zero axis to the point "x" was also measured in cm as squares and converted to volts. This distance in volts was called $E_{d.e.}$. A plot of $E_{d.e.}$ versus $\log(i_d - i)/i$ was made. $n\alpha$ was determined from the slope of the line, on the assumption that the following equation was applicable.

$$E_{d.e.} = E_{\frac{1}{2}} - 0.0591/n\alpha \log(i_d - i)/i$$

RESULTS

Most polarograms were well defined, except those of the alcoholic solutions which at high pH values showed a very small plateau.

A.- Current versus Concentration:-

Within the range studied, the current was found directly proportional to concentration. The concentration range is given in Table, 1. For aqueous solutions, concentrations higher than 1.5×10^{-3} Molar gave polarograms with irregular maxima.

For the same compound the slope (i_d/C $\mu\text{a}/\text{mmole}$) of the plot current versus concentration was not constant for different pH values. Tables 2,3,4. The variations were most pronounced for N-Nitroso-dimethylamine at pH 3.74 and for N-Nitroso-piperidine appeared only at pH 2.27, yet plots of i_d versus C gave in both cases as good a straight line passing through the origin as in any of the other cases. Fig. 2,3. The variation of i_d/C with pH for N-Nitroso-diphenylamine is not pronounced.

Since N-Nitroso-diphenylamine had to be studied in alcoholic solution N-Nitroso-dimethylamine and -piperidine were studied in the same solvent, at pH 4 for comparison. The i_d/C values are given in Table 5.

B.- Half-Wave Potential:-

The cell resistance was found to be 200 ohms for aqueous solutions and 250 ohms for alcoholic solution. In both cases the IR drop of the cell was within the range of experimental error.

The half-wave potential in the three compounds was found to vary linearly with pH. Fig. 4,5. With N-Nitroso-piperidine and -dimethyl the change of slope about pH 4 is pronounced. The slopes of the straight lines till pH 4 are 0.07 volt / pH and 0.10 volt /pH respectively. For N-Nitroso-diphenylamine the slope of the straight line within the range studied is 0.10 volt / pH.

The high side of the pH range was limited in all compounds by the hydrogen wave. This limitation was most pronounced in the case of N-Nitroso-diphenylamine because of the second wave of oxygen (ca. 1.22 volt).

At the low side of the range; below pH 1.15, the first wave of oxygen (ca. 0.15 volts) came close to that of N-Nitroso-diphenylamine and the curve was not well defined, below pH 1.89 N-Nitroso-piperidine had a maximum, below pH 1.41 N-Nitroso-dimethylamine also had a maximum.

Generally $E_{\frac{1}{2}}$ fluctuated with concentration, but at a given concentration the results were reproducible. With the precision of the instrument and the variations due to liquid junction potential for the alcoholic solutions, it was not possible to interpret the results. The $E_{\frac{1}{2}}$ values

reported in Tables 3,4,5 are the average of different concentrations at the same pH. The deviation from the average was less than 0.03 volts.

C.- Calculations of $n\alpha$, the number of electrons (n) and α :

The variation of $n\alpha$ with pH was found regular, and inversely proportional to pH. Tables 2,3,4.

The number of electrons (n) was calculated from the Ilkovic equation. In all calculations $m^{2/3} t^{1/6}$ was taken as $\frac{3.21^{2/3}}{2.32^{1/6}} = 2.504$. The diffusion coefficients were taken as⁽¹⁴⁾,

N-Nitroso-dimethylamine	$D = 8.5 \times 10^{-6} \text{ cm}^2 \text{ sec}^{-1}$
N-Nitroso-piperidine	$D = 8.0 \times 10^{-6} \text{ cm}^2 \text{ sec}^{-1}$
N-Nitroso-diphenylamine	$D = 3.3 \times 10^{-6} \text{ cm}^2 \text{ sec}^{-1}$

On the assumption that the change in the diffusion coefficient due to change in solvent was small the same diffusion coefficient was used in all cases.

i_d/C was read from the plot of i_d versus C, then n was calculated as,

$$n = \frac{1}{605 D^{1/2} m^{2/3} t^{1/6}} \times \frac{i_d}{C}$$

The variations of n with pH were generally small, and without trend. For N-Nitroso-dimethylamine the n values were random between 3.42 - 5.30. Table 2. For

14. Private Communication from Dr. J. Heyrovsky.

N-Nitroso-piperidine n was found to be about four at all pH values studied except pH 2.24 where it was 5.56. Table 3. For N-Nitroso-diphenylamine, n had a random distribution around four.

The number of electrons in the reduction of N-Nitroso-dimethylamine and -piperidine were also determined in 50% ethyl alcohol as solvent. Table 5.

On the assumption that the reduction of the N-Nitroso-compounds obeys the Ilkovic equation and the calculated average value of n is meaningful, α was calculated from $n\alpha$ with results shown in Tables 2,3,4,5.

D.- Temperature Experiment:-

The temperature coefficient $1/i \, di/dt$ was small. Table 6. Fig. 6. $E_{1/2}$ varied slightly with temperature. For N-Nitroso-piperidine the trend was towards more negative potentials for rise in temperature. A similar but less pronounced trend was observed with N-Nitroso-dimethylamine. In case of N-Nitroso-diphenylamine the variation was random. Table 6.

E.- Height Experiment:-

The height experiment was carried on for N-Nitroso-piperidine in aqueous solvent. The change of current at different potentials due to change of the height (h) of the mercury column was observed.

A direct relation of current with \sqrt{h} was found. At the foot of the wave, the increase of current with \sqrt{h} was

more pronounced than at the head of the wave.

The half-wave potential was constant at different values of (h) .

DISCUSSION

A.- Elucidation of the Controlling Step of the Reduction

Mechanism:•

The fact that i_d is proportional to the concentration does not necessarily imply that the reduction is only diffusion controlled and follows the Ilkovic equation. Some "rate-controlled" processes also give such a relationship. For example, in the reduction of formaldehyde i_d is proportional to the concentration, yet it has been shown by K. Vesely⁽¹⁵⁾ that the current depends on the rate of dehydration of $\text{CH}_2(\text{OH})_2$. A similar behavior is observed with pyruvic and phenylglyoxylic acids.

Since i_d/C is not constant at different pH's but fluctuates without drift, then either the Ilkovic equation is not obeyed or else the type of reduction mechanism varies irregularly. It could also be argued that since the variation has no trend there are more than one factor influencing this fluctuation.

The variation of the current with the height of the

15. Vesely, K. and Brdicka, R., Collection Czechoslov. Chem. Commun., v. 12, (1947) p. 39 and 148.

mercury head often helps the study of the rate determining step. Since m (the weight of each drop of mercury in mg) is directly proportional to h , and t (the drop time in seconds) is inversely proportional to h , then it follows from the Ilkovic equation that i_d is directly proportional to \sqrt{h} . For N-Nitroso-piperidine this relation was found almost linear at all points of the graph. This denotes a diffusion controlled process.

Further support to the diffusion controlled process is given by the behavior of i_d with temperature. In all three compounds the temperature coefficient was found smaller than 2% and this is usual for diffusion controlled currents. However, D. Stocesova⁽¹⁶⁾ has shown that the second wave of nitrobenzene, which corresponds to the irreversible reduction of phenylhydroxylamine to aniline, does not depend on the temperature.

J. Page⁽¹⁷⁾ reports that a change in $E_{1/2}$ of 1 mv per degree is normal for diffusion controlled processes. As shown in Table 6. the variation of $E_{1/2}$ with temperature is more than 1 mv.

All these arguments show that the process could be exclusively diffusion controlled, or else could be controlled by a combination of diffusion and reaction rate

-
16. Stocesova, D., Collection Czechoslov. Chem. Commun., v. 12, (1949) p. 64.
17. Page, E.J., op.cit. p. 270.
-

with the latter the less effective.

B.- The Reduction Mechanism is Irreversible:-

The plot of i versus E is symmetrical, as shown in Fig. 1. But a symmetrical curve is observed in both reversible and irreversible processes.

The clue to the irreversibility of the wave is based on two observations:-

1.- The plot of $E_{d.e.}$ versus $\log(i_d-i)/i$ gives a straight line which obeys the following equation:

$$E_{d.e.} = E_{\frac{1}{2}} - 0.0591/n\alpha \log(i_d-i)/i \text{ at } 25^\circ\text{C}$$
$$n\alpha \text{ being less than one. Fig. 7.}$$

2.- $E_{\frac{1}{2}}$ varies with concentration.

Of those two indications the first is the more reliable.

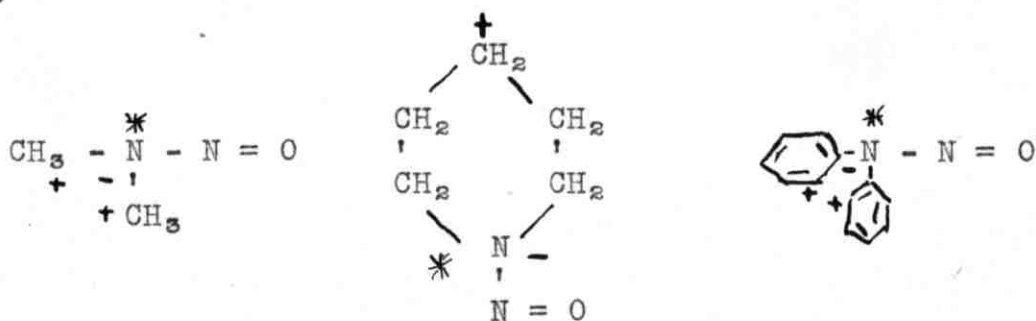
The linear variation of $E_{\frac{1}{2}}$ with pH does not help to determine the type of process, since this relationship is observed in both reversible and irreversible processes.

C.- The Steps of the Mechanism of the Reduction:-

All the following observations, a symmetrical S-shaped curve, a linear relationship of $E_{\frac{1}{2}}$ with pH and an irreversible wave, permit the classification of the reduction as "type one" mentioned by J. Page and discussed on page 5 of this thesis. Either there is a direct electron transfer between the electrode and the organic compound but the reaction product is unstable and is consumed, or else the equilibrium at some point of the process is reached slowly.

If it is assumed that the calculated values of n for N-Nitroso-dimethylamine, -piperidine and -diphenylamine in 50% ethyl alcohol are meaningful, that is, 3, 3 and 5 respectively, then α is approximately the same for N-Nitroso-dimethylamine and -diphenylamine, but it is higher for N-Nitroso-piperidine. If n is taken as 2,2,4 then α still holds approximately the same relation. Table 5.

If α is defined as the fraction of potential necessary for reduction, then the above mentioned results would imply that N-Nitroso-dimethylamine and -diphenylamine require approximately the same amount of energy for reduction while N-Nitroso-piperidine must be supplied with more energy.

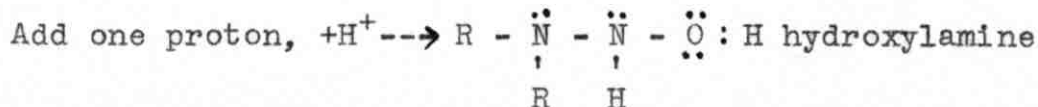
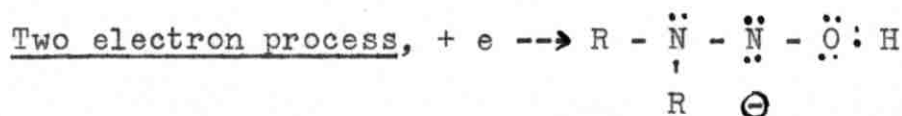
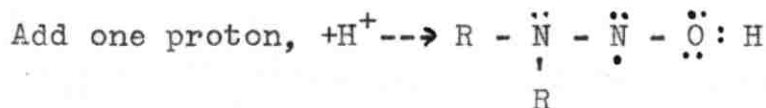
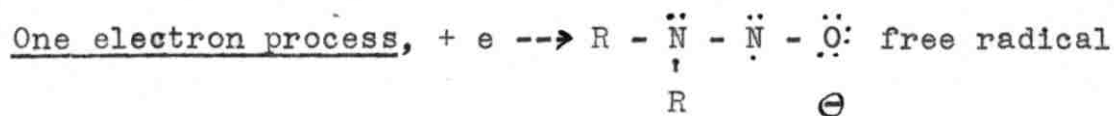
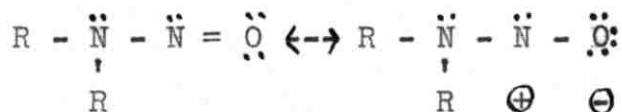


Since α for N-Nitroso-diphenylamine and N-Nitrosodimethylamine are almost the same, the phenyl group could be regarded as electron donating group as well as the methyl group. From the three formulas above it is clear that the N-Nitroso-piperidine molecule as a whole has more di-pole character than the N-Nitrosodimethylamine or -diphenylamine. For the latter two compounds the centre of gravity of the

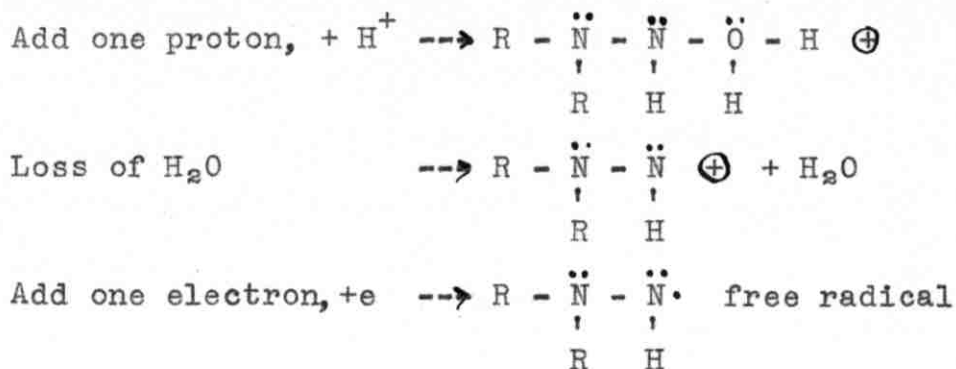
plus charges almost coincides with that of the minus charges. Because of this difference in polarity the nitro-genated group is more negative for N-Nitroso-piperidine than for the other two.

The difference in the negative character of the nitrogen and the fact that α for N-Nitroso-piperidine is larger than the others permits the assumption that in the acceptancy of an electron and a proton, the attack of the electron could be the determining step in the reduction.

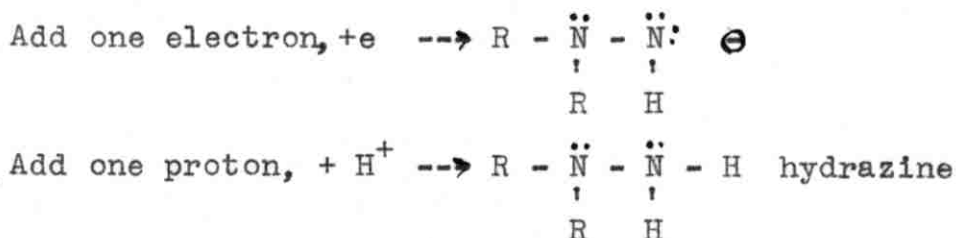
On the basis of the above discussion the following mechanism could be presented:-



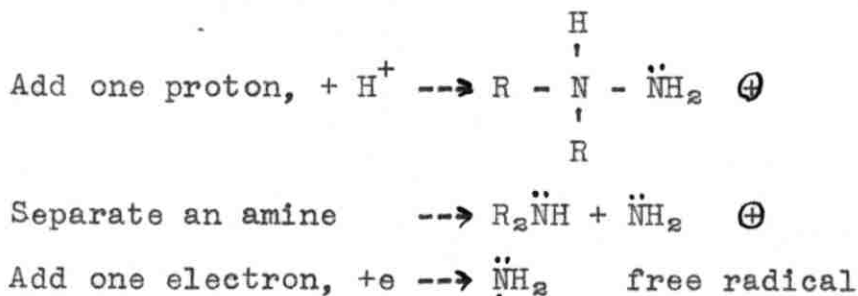
Three electron process: Hydroxylamine cannot accept an electron. The reduction proceeds by acceptance of a proton by the electron rich oxygen.



Four electron process,



Five electron process: The left nitrogen is the richer in electrons, because it bears two electropositive groups.



At each odd stage, the free radical could be stabilised by doubling; this would stop the reduction at that stage. The reduction with six electrons would give NH_3 instead of $\text{NH}_2\text{-NH}_2$.

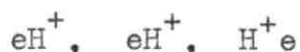
The n values calculated from the Ilkovic equation are without trend. There could be two interpretations:-

- 1.- The determining step of the reduction is not

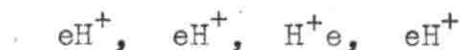
exclusively diffusion of the reaction material but a combination of reaction rate and diffusion.

2.- The determining step in diffusion only and the number of electrons in the reduction are at certain pH's 4 and at others 5.

For N-Nitroso-dimethylamine and -piperidine the n value 3 in 50% ethyl alcohol could be interpreted as reduction with doubling up of two free radicals.

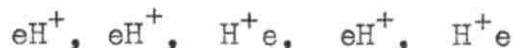


The product of a 4 electron reduction is a hydrazine derivative which is not a very stable compound.



For 5 electron reduction the hydrazine derivative is reduced further to the corresponding amine and $\cdot\ddot{N}:H$,
 \ddot{H}

with the latter doubling up to give NH_2-NH_2 .



The easy transition from 4 to 5 electron processes could be a reason for the random values of n .

Table 1

Concentration Range

<u>N-Nitroso-</u>	<u>Solvent</u>	<u>Concentration x 10⁴ moles/liter</u>
- dimethylamine	water	3.35 - 14.87
- piperidine	water	3.55 - 8.87
- diphenylamine	50% ethyl alcohol	4.77 - 24.70

Table 2

N-Nitroso-dimethylamine at 30°C
in water and 0.1N KCl

pH	i_d/C µa/mmole	$E_{1/2}$ volts(S.C.E.)	$n\alpha$	n	n	n	$n\alpha/4$	$n\alpha/5$
						integer		
1.41	23.4	0.90	0.77	5.30	5		0.19	0.16
2.69	17.4	1.01	0.72	3.94	4		0.18	0.14
2.80	17.1	1.04	0.71	3.87	4		0.18	0.14
3.37	22.2	1.09	0.67	5.03	5		0.17	0.13
3.74	15.1	1.12	0.60	3.42*	3		0.15	0.12
4.00	22.6	1.15	0.47	5.12	5		0.12	0.09
4.22	19.6	1.19	0.47	4.44	4		0.12	0.09
4.34	17.5	1.23	0.43	3.94	4		0.11	0.09

Average value of $n = 4.5 \pm 0.5$

$n = 4$ or 5

* Not included in the average

Table 3

N-Nitroso-piperidine at 25°C

in water and 0.1N KCl

pH	i_d/C $\mu\text{a}/\text{mmole}$	$E_{1/2}$ volts (S.C.E.)	$n\alpha$	n	n	n $\alpha/4$	n $\alpha/5$
					integer		
1.89	17.5	0.83	0.79	4.08	4	0.20	0.16
2.24	23.8	0.86	0.80	5.55*	5	0.20	0.16
3.97	-	0.96	0.75	-	-	0.19	0.15
4.50	18.0	1.02	0.58	4.20	4	0.14	0.12
4.96	17.6	1.09	0.56	4.11	4	0.14	0.12

Average value of $n = 4.13 \pm 0.05$

$n = 4$

* Not included in the average

Table 4

N-Nitroso-diphenylamine at 25°C
in 50% ethyl alcohol
and 0.1N KCl

pH	i_d/C $\mu a/mmole$	$E_{1/2}$ volts (S.C.E.)	$n\alpha$	n	n	$n\alpha/4$	$n\alpha/5$
				integer	integer		
1.15	13.0	0.56	1.03	4.73	5	0.26	0.21
2.51	10.2	0.69	1.03	3.71	4	0.26	0.21
3.93	13.4	0.83	0.78	4.87	5	0.19	0.16
4.66	10.1	0.88	0.92	3.67	4	0.23	0.18
5.27	12.3	0.92	0.89	4.47	4	0.22	0.18

Average value of $n = 4.3 \pm 0.6$

Table 5

N-Nitroso compounds at 25°C
in 50% ethyl alcohol & 0.1N KCl

N-Nitroso-	pH	i_d/C $\mu a/mmole$	$E_{1/2}$ volts(S.C.E.)	$n\alpha$	n	n integer	α_1^*	α_2^{**}
-dimethyl- amine	4.06	11.5	1.23	0.44	2.83	3	0.15	0.22
-piperidine	4.06	11.9	1.08	0.69	2.80	3	0.23	0.35
-diphenyl- amine	3.93	13.40	0.83	0.77	4.87	5	0.15	0.19

* α_1 for $n = 3, 3, 5$ respectively

** α_2 for $n = 2, 2, 4$ respectively

Table 6
Temperature Experiment

N-Nitroso-	-dimethylamine	-piperidine	-diphenylamine
pH	4.34	4.58	5.42
1/idi/dtx100 at 25°C	0.80%	1.52%	2.3%
Temperature °C	$E_{\frac{1}{2}}$ volts (S.C.E.)	$E_{\frac{1}{2}}$ volts (S.C.E.)	$E_{\frac{1}{2}}$ volts (S.C.E.)
10	-	-	0.577
12	-	1.014	-
15	-	1.018	-
16	-	-	1.014
20	-	1.026	1.039
25	1.237	1.026	0.910
30	1.236	1.033	0.921
35	1.248	-	-

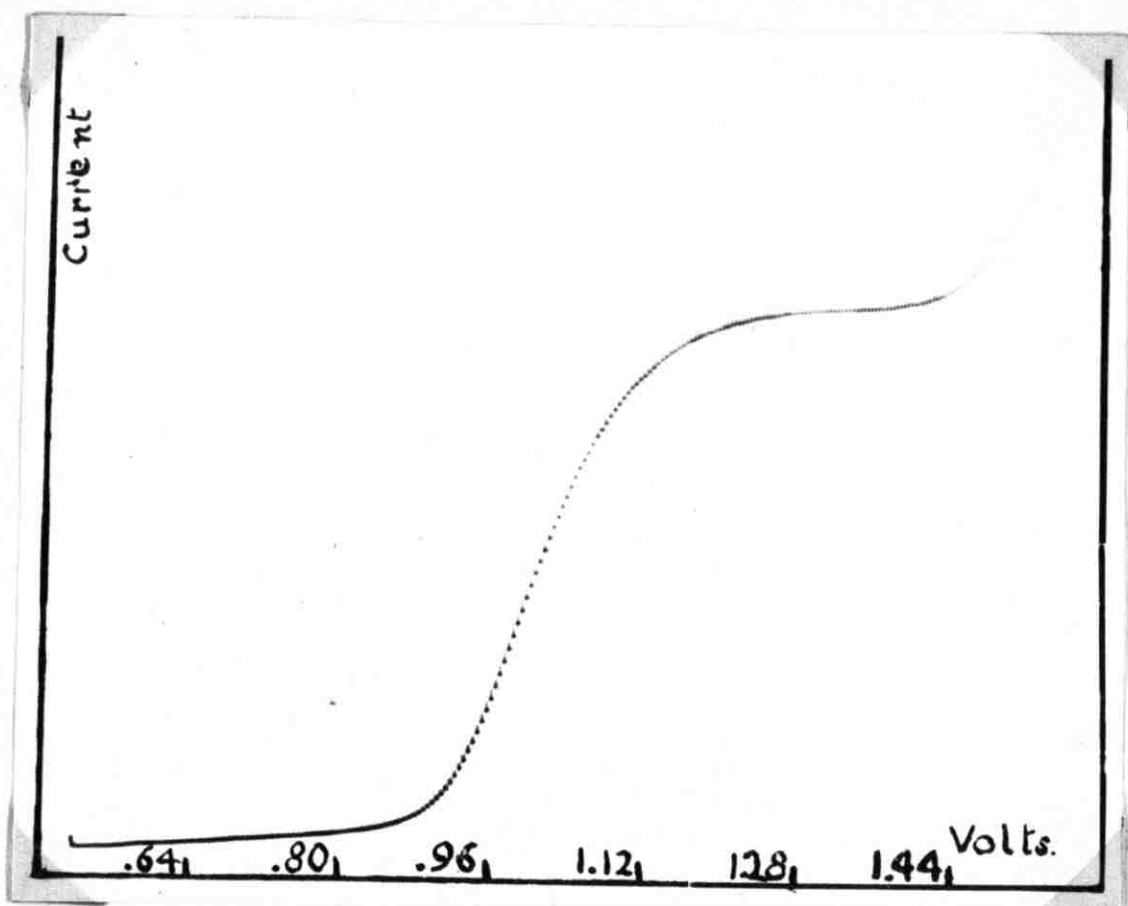


Fig. 1. - N-Nitroso-piperidine
 1.19×10^{-3} M
0.1 N. KCl
pH 4.96.

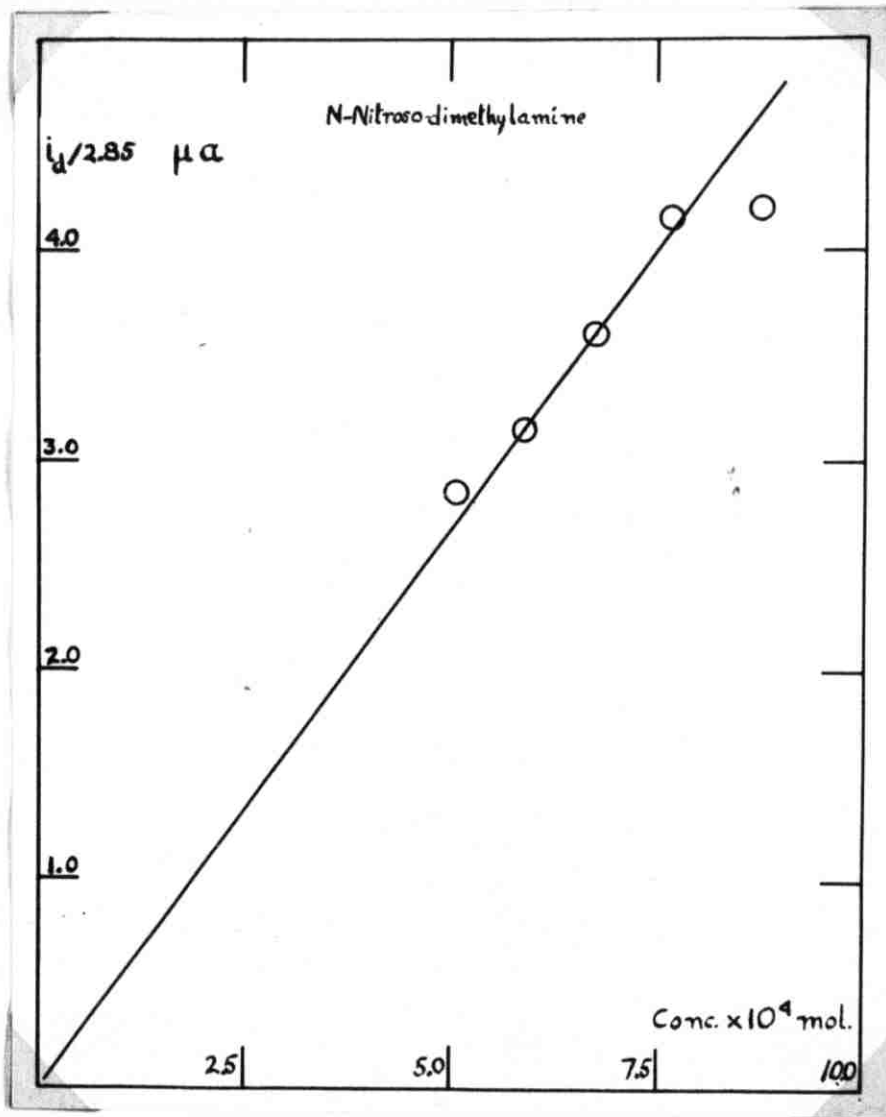


Fig. 2.- In 0.1N KCl, at pH 3.74.

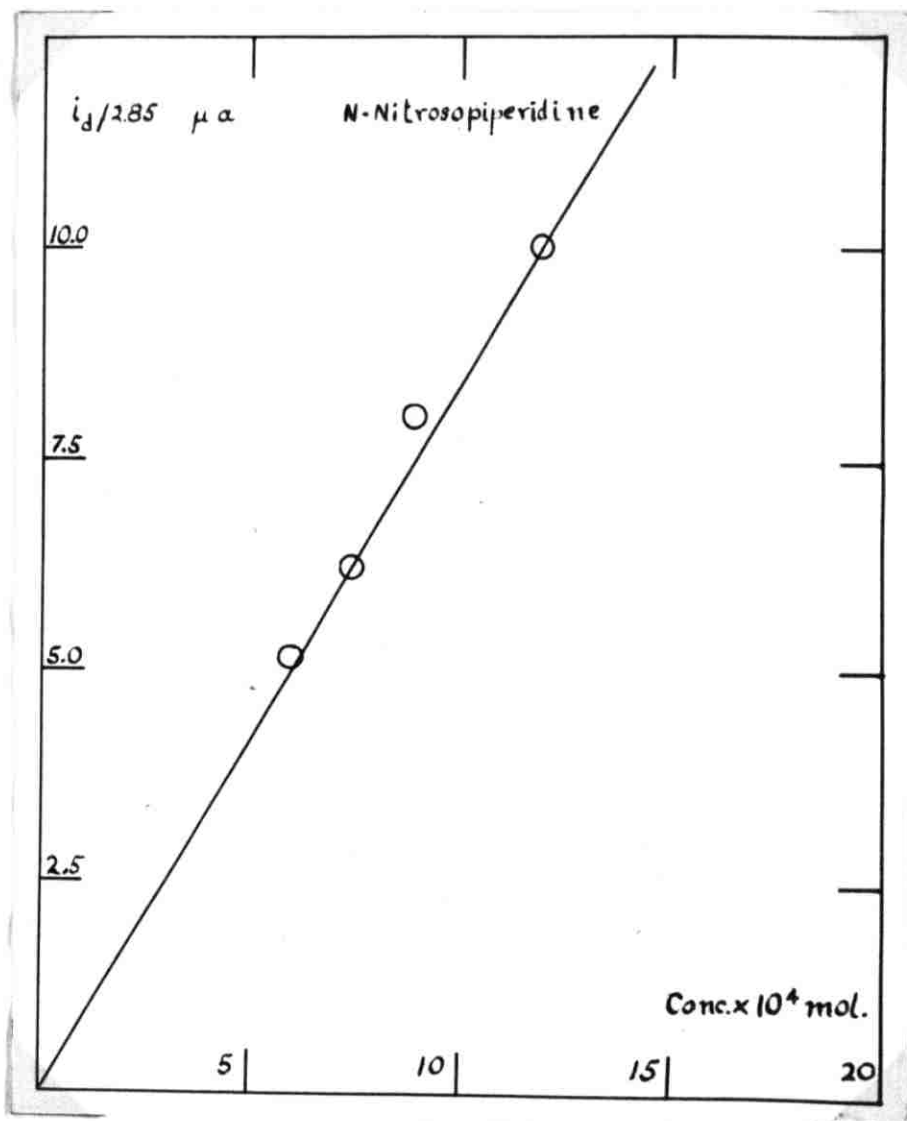


Fig. 3.- In 0.1N KCl, at pH 2.27

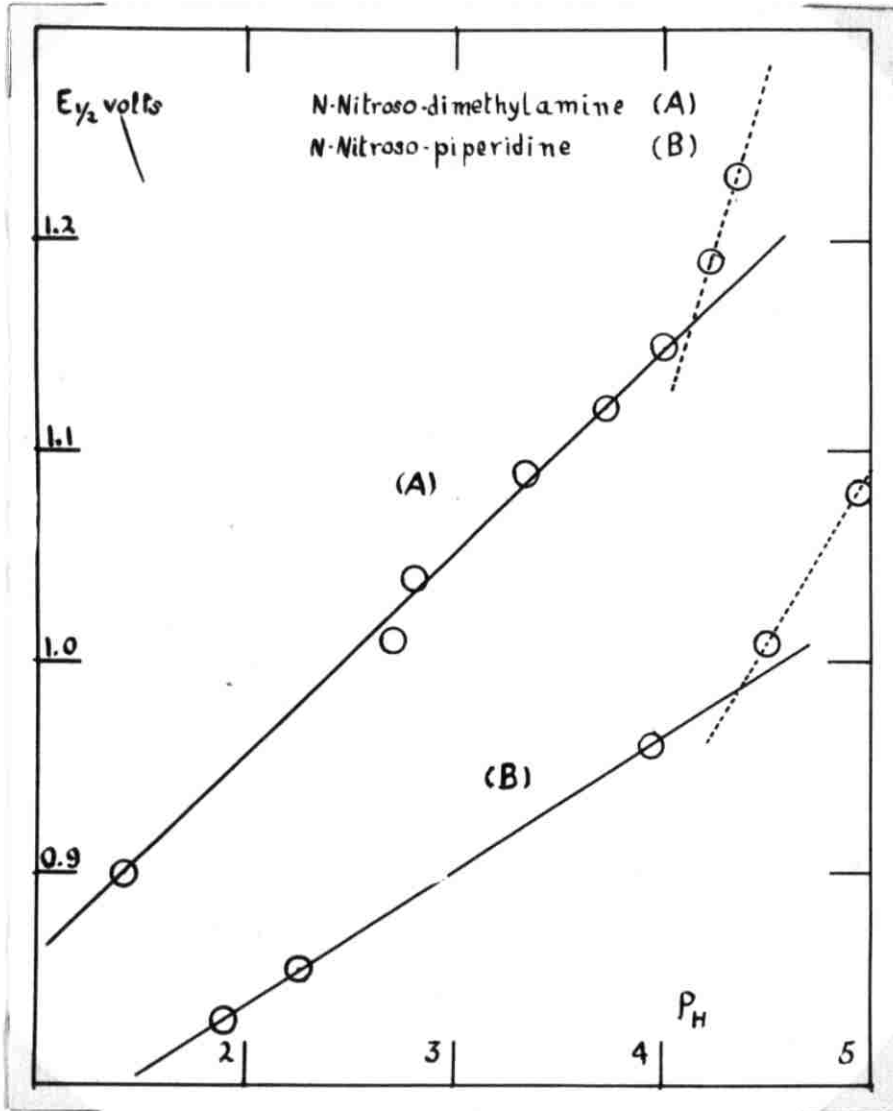


Fig. 4..

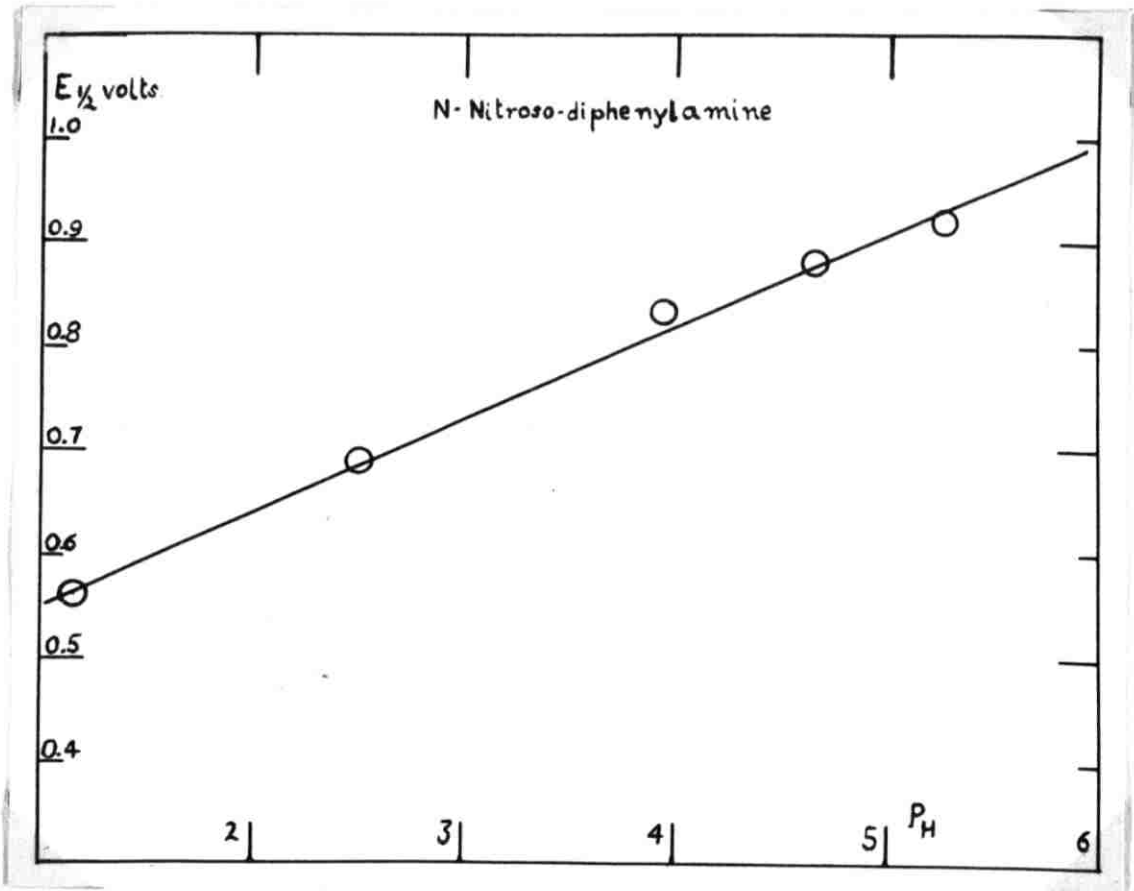


Fig. 5..

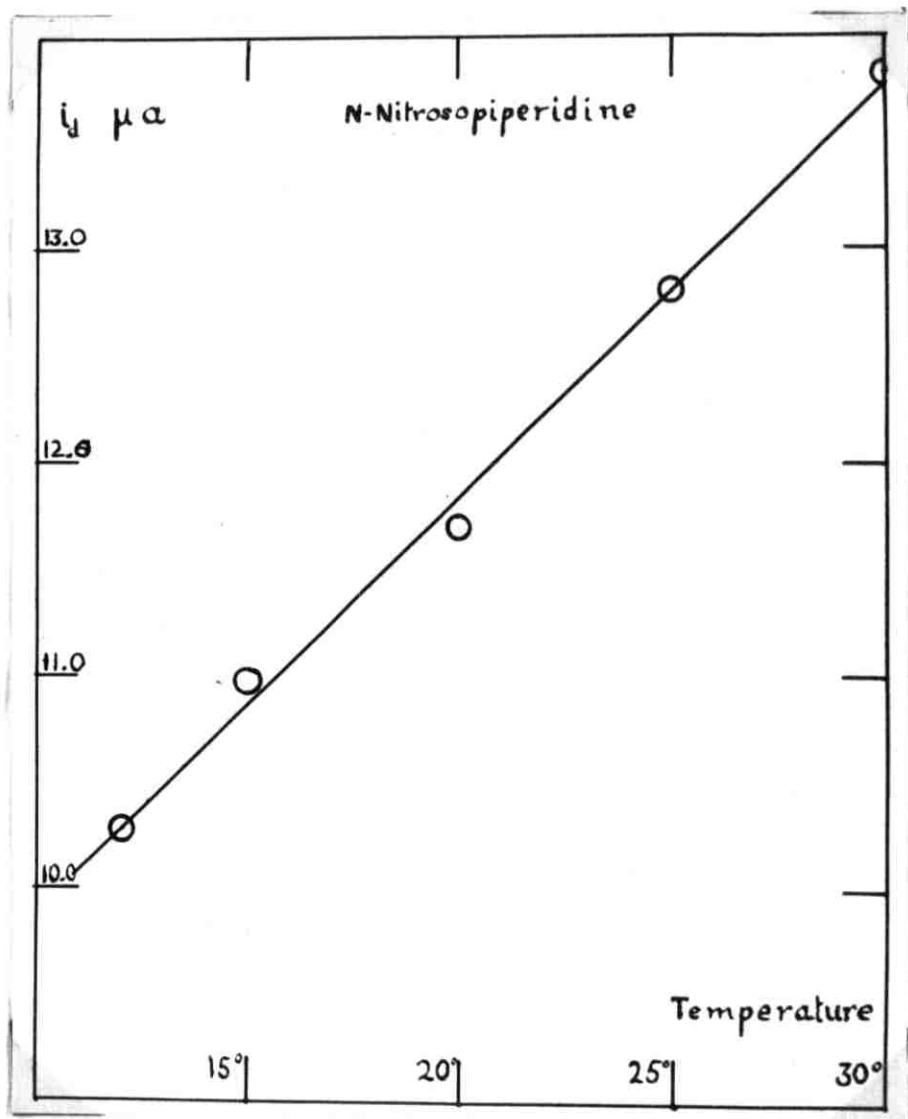


Fig. 6.- at pH 4.06.

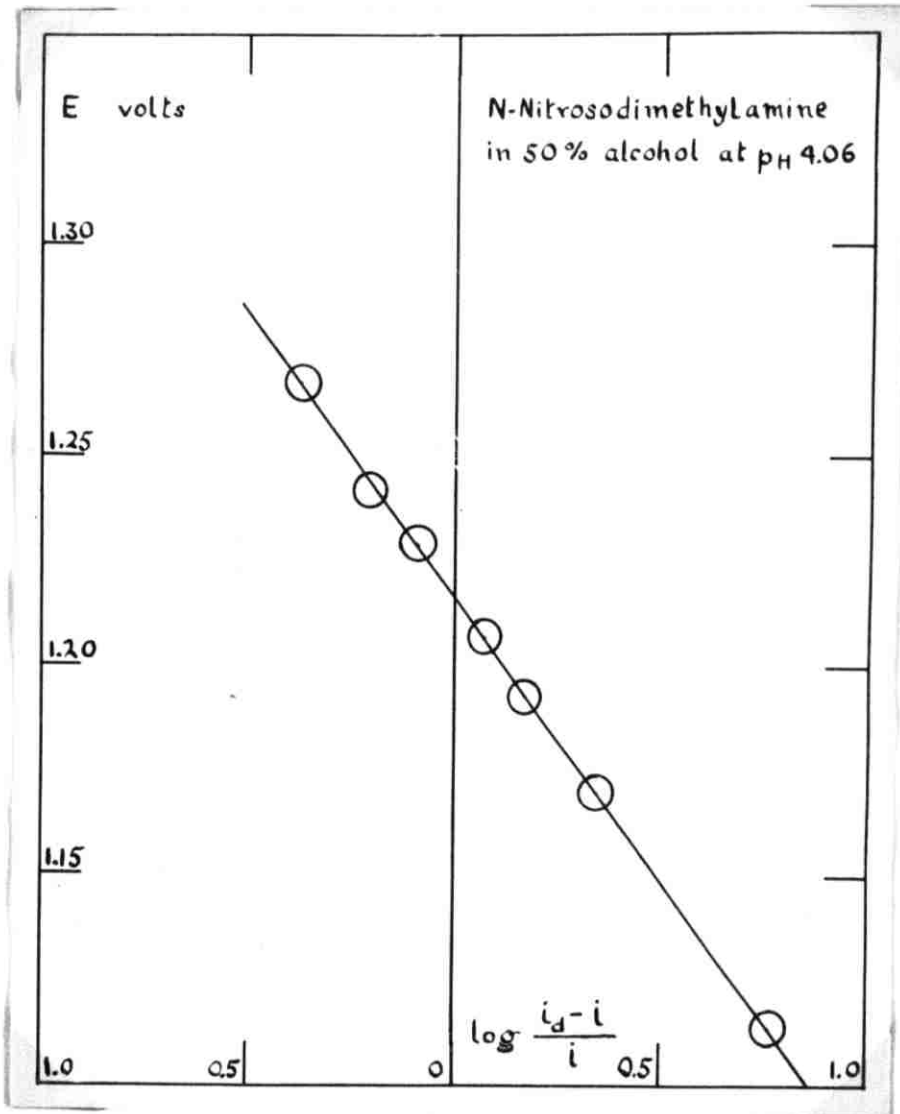


Fig. 7.-

BIBLIOGRAPHY

- 1.- Brdicka, R. et al. Collection Czechoslov. Chem. Commun., v. 12, 138 (1947).
- 2.- Britton, S.T.H., Hydrogen Ions. p. 217, London, Chapman and Hall LTD., 1932.
- 3.- Charles, D.C., ed. Handbook of Chemistry and Physics. p. 778. Cleveland, Ohio, Chemical Rubber Publishing Co., 1946.
- 4.- Deutschen Chemischen Gesellschaft, ed. Beilsteins Handuch Der Organischen Chemie, v. 20, p. 83. Berlin, Julius Springer 1935.
- 5.- Eyring, H. et al. J. Phys. & Colloid Chem., v. 53, 1453 (1949).
- 6.- Gardner, J.H. et al. Reviews of Pure and Applied Chemistry, v. 3, 134 (1953).
- 7.- Hickinbottom, J.W., Reactions of Organic Compounds. p. 286, London, Longmans, Green and Co., 1945.
- 8.- Kivalo, P. et al. J. Am. Chem. Soc., v. 75, 4148, (1953).
- 9.- Kolthoff, I.M. et al. J. Am. Chem. Soc., v. 71, 3916 (1949).
- 10.- _____., Polarography. v. 1 and 2., New York, Interscience Publishers, 1952.
- 11.-Laitinen, H.A. et al. J. Am. Chem. Soc., v. 64, 1765 (1942).

- 12.- Muller, H.O., The Polarographic Method of Analysis.
Easton, Pa., Chemical Education Publishing Co.,
1951.
- 13.- Page, E.J., Quarterly Reviews, v. 6, 262 (1952).
- 14.- Pearson, J., Trans. Faraday Soc., v. 44, 683 (1948).
- 15.- Stocesova, D., Collection Czechoslov. Chem. Communs.,
v. 14, 615 (1949).
- 16.- Vesely, K. et al. Collection Czechoslov. Chem.
Communs., v. 12, 313 (1947).
- 17.- Wawzonek, S., Annual Review of Physical Chemistry,
v. 3, 247 (1952).
- 18.- Willard, H.H. et al. Instrumental Methods of Analysis.
p. 292, New York, D. Van Nostrand Company, Inc.,
1952.