$$CH_3NCS + CH_3NH_2 \longrightarrow (CH_3NH)_2CS \quad (3)$$

is also most probably involved.

The finding that tetramethylthiourea does not decompose establishes that a hydrogen atom bonded to nitrogen is necessary for decomposition to take place. It also provides additional strong support for the conclusion previously presented[3] that methyl groups do not migrate and that decomposition takes place by intramolecular hydrogen transfer and dissociation of the activated complex.

A more detailed theoretical interpretation of this and other data will be presented in the last paper of this series.

**Acknowledgment.**—The authors gratefully acknowledge the generous grant from the Research Corporation of New York that made this study possible. It is also a pleasure to express our thanks to the Humble Oil & Refining Company for the fellowship awarded to D.G.W.

AUSTIN 12, TEXAS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF KENTUCKY]

# The Polarography of Quinoxaline[1]

BY MURRAY P. STRIER AND J. C. CAVAGNOL[2]

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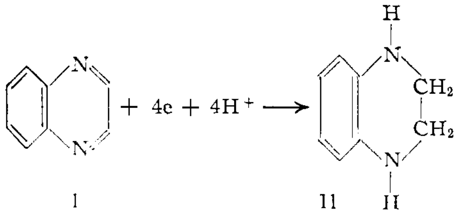
The reductions of quinoxaline at the dropping mercury electrode, conducted in buffered media in the *p*H range of 1 to 10, show well-defined, *p*H dependent waves. The influence of variations in buffer components, concentration and ionic strength on the nature of the waves have been investigated. The course of the reduction at all *p*H levels is not affected by changes in buffer components, buffer concentration or ionic strength. However, certain variations in half-wave potentials and diffusion current constants occur. Reduction to 1,4-dihydroquinoxaline is postulated for the whole *p*H range. From *p*H 1 to *p*H 2 reduction may proceed by a bimolecular, one-electron process that is not completely reversible. Reduction may also proceed by this process at *p*H 3 but this is apparently not true as the concentration of buffer components is increased. Over the *p*H range of 4 to 10 the simultaneous addition of two protons and two electrons is presumed to occur in an essentially reversible manner. Catalytic hydrogen waves are manifested following the formation of dihydroquinoxaline at *p*H's < 7 but are absent at higher *p*H's. At *p*H 7 the catalytic wave appears only at high buffer concentration.

## Introduction

The polarography of quinoxaline (I) was undertaken in order to determine whether 1,2,3,4-tetrahydroquinoxaline (II) could be obtained by electrochemical methods. The over-all reduction is represented by



(1)

I II

The literature on polarography involving reduction at the dropping mercury electrode contains only two references to simple quinoxalines. Winkel and Proske[3] obtained a polarographic wave for 2,3-dimethylquinoxaline in 0.1 *M* ammonium chloride solution, but no analysis is given. Sartori and Furlani[4] studied the polarographic reduction of quinoxaline, its methiodide and its di-N-oxide. They found that quinoxaline gives a nearly reversible, 2-electron wave having an $E_{0.5}$ of $-0.267$ v. S.C.E. at *p*H 0 and 25°. Both prewaves and kinetic waves were found, in agreement with the present work. The formation of dihydroquinoxaline and the absence of the tetrahydro form were postulated. The roles of ionic strength and buffer composition were minimized, in contrast to the present paper.

Equation 1 demonstrates that *p*H is a critical factor in governing the reduction process. The need for employing buffered solutions having adequate ionic strength as supporting electrolytes has been stressed elsewhere.[5] Quinoxaline was studied systematically by varying buffer components, ionic strength, buffer concentration, *p*H and reductant concentration.

## Experimental

**Materials.**—Quinoxaline was prepared by the method of Cavagnol and Wiselogle.[6] The product, resublimed prior to use was colorless and melted at 31.0–31.5°. It was used in the form of a 0.010 *M* stock solution stored under nitrogen in the dark. All supporting electrolyte components were C.P. grade and the suitability for polarographic work was established by blank runs.

Stock solutions of 0.110 *N* sodium hydroxide and 0.205 *N* hydrochloric acid were prepared and stored under nitrogen.

**Apparatus.**—A manual instrument of the type described by Kolthoff and Lingane[7] was used. Both the applied potential and the resulting current (as the potential across a 10,000-ohm precision resistor) were measured with a Leeds and Northrup student-type potentiometer. With this apparatus, solutions of $5.8 \times 10^{-4}$ *M* cadmium sulfate in 0.100 *M* potassium chloride gave an $E_{0.5}$ value of $-0.597 \pm 0.001$ v. *vs.* S.C.E. and an $I_d/Cm^{2/3}t^{1/6}$ value of $3.38 \pm 0.02$ at 25°.

All measurements were performed in a 100-ml. Berzelius

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[1] Abstracted from a dissertation submitted to the Graduate School by Murray P. Strier in partial fulfillment of the requirements for the degree of Doctor of Philosophy, Jan. 1952.

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[3] A. Winkel and G. Proske, *Ber.*, **69**, 1917 (1936).

[4] G. Sartori and C. Furlani, *Ann. chim. (Rome)*, **45**, 251 (1955), *C. A.*, **49**, 15557b.

[5] J. J. Lingane, THIS JOURNAL, **61**, 2099 (1939); N. H. Furman and K. G. Stone, *ibid.*, **70**, 3055 (1948); P. J. Elving and C. Teitelbaum, *ibid.*, **71**, 3916 (1949); P. J. Elving and C. S. Tang, *ibid.*, **72**, 3918 (1950); P. E. Stewart and W. A. Bonner, *Anal. Chem.*, **22**, 793 (1950); P. J. Elving, K. C. Komyathy, R. E. Van Atta, C. S. Tang and I. Rosenthal, *ibid.*, **23**, 1218 (1951).

[6] J. C. Cavagnol and F. Y. Wiselogle, THIS JOURNAL, **69**, 795 (1947).

[7] I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1946, Chapter XIV.

beaker thermostated at 25 ± 0.05°. A saturated calomel electrode, stored permanently in the constant temperature bath, served as the reference electrode. This electrode was connected to the electrolysis cell by means of a saturated potassium chloride–agar bridge fitted with a sintered glass tip. Two capillaries, prepared from Corning marine barometer tubing, delivered mercury into distilled water at rates of 2.09 and 2.14 mg. sec.$^{-1}$. The height of the mercury column was fixed at 58.0 cm. for all measurements.

The *p*H measurements were made with a Beckman Model G *p*H meter and all resistances were measured with a Serfass Conductance Bridge, Model RC M15.

**Procedure.**—Preliminary experiments showed that the most suitable working range of the instrument was from 1 to 7 ma. Under these conditions the half-wave potentials were reproducible to ±2 mv. and the diffusion current constants varied less than ±1%.

The constituents of the Clark and Lubs buffer system were used in the *p*H range of 1 to 9. In order to study the effect of the reduction wave, it was necessary to employ other buffer systems. At *p*H 1 and *p*H 2 potassium hydrogen sulfate was substituted. Sodium hydrogen tartrate was used at *p*H 3 and the phosphate buffer system served well at *p*H 10. The concentrations of buffer salt (acid) were varied from 0.05 to 0.8 *M* with ionic strengths being 0.05 to 1.4 *M*.

Test solutions containing buffer components other than Clark and Lubs were prepared as follows. The appropriate solid buffer was weighed, dissolved in distilled water and standard acid or base added until the desired *p*H was reached. Sufficient potassium chloride or sodium chloride then was added to bring the ionic strength to the desired level. A final adjustment of *p*H was made by adding standard acid or base. Gelatin was added as maximum suppressor from a stock solution so that after dilution to volume (100 ml.), its concentration was 0.01%. Finally, quinoxaline stock solution was added to obtain the desired concentration without changing the *p*H.

Current and applied potential measurements were made in an atmosphere of purified nitrogen. After scanning the complete working range at 0.1 v. intervals and plotting the data, intermediate points were taken at 0.01 v. intervals. The mercury drop time was measured at 0.1 v. intervals over the significant portions of the wave. At the conclusion of each polarogram the cell resistance was determined to correct the half-wave potential for *iR* drop across the cell.

## Results

In Table I are summarized the results obtained for the reduction of 4.5 × $10^{-4}$ *M* solutions of quinoxaline in two different buffer systems. The first buffer system employed is the Clark and Lubs buffers and will be designated henceforth as the "Low" buffers. The second buffer system, designated as the "High" buffers, is characterized by having a higher concentration of buffer components and ionic strength than the "Low" buffers at all *p*H's. The level of ionic strength for the "High" buffers is 0.6 *M* and the *p*H range covered is 1 to 10. The *p*H range covered with the "Low" buffers is 1 to 9.

Two major waves are obtained for quinoxaline over the *p*H range of 1 to 7. Only the first major wave is present at *p*H's > 7. The second major wave is not evident at *p*H 7 in the "Low" buffer and is measured with difficulty at this *p*H in the "High" buffer. The first major wave is partially differentiated into two equal segments at *p*H 1 and *p*H 2 in each buffer system but this is less distinct at *p*H 2. At *p*H 3 faint evidence of differentiation for the first major wave exists in the "Low" buffer but not in the "High" buffer. Some differentiation of the second major wave occurs in the "Low" buffers at *p*H 1 and *p*H 2, but this vanishes with increasing buffer concentration.

Generally, the concentration of quinoxaline was varied from 2.5 × $10^{-4}$ *M* to 7.0 × $10^{-4}$ *M* in both "Low" and "High" buffers. Also at each *p*H the effect of such variables as buffer constituents, concentrations and ionic strengths[8] on the nature of the polarographic waves, half-wave potentials and diffusion current constants were ascertained for 4.5 × $10^{-4}$ *M* solutions of quinoxaline. The results obtained can be given[9] briefly as follows:

**A. First Major Wave.**—At *p*H 1 the half-wave potential remains constant as the concentration of potassium hydrogen sulfate is varied from 0.400 to 0.800 *M* with an accompanying increase in ionic strength from 0.620 to 1.43 *M*. No uniform variations in half-wave potentials with increased buffer concentration and ionic strength can be discerned at *p*H 2. At *p*H 3 there is no apparent change in half-wave potential in going from 0.050 *M* potassium hydrogen phthalate buffer to 0.050 *M* sodium hydrogen tartrate buffer. Increasing the concentration of sodium hydrogen tartrate at this *p*H to 0.300 *M* leads to decreasingly negative half-wave potentials. Either increasing the ionic strength to 0.601 *M* by addition of neutral salt or increasing the concentration of sodium hydrogen tartrate to 0.400 *M* while maintaining the ionic strength constant at 0.601 *M* has no further influence on the half-wave potential. At *p*H 4 the half-wave potential varies from −0.488 to −0.480 v. as the concentration of potassium hydrogen phthalate increases from 0.050 to 0.250 *M* with the ionic strength increasing from 0.050 to 0.258 *M*. The half-wave potential then remains constant as the concentration of potassium hydrogen phthalate is increased to 0.450 *M*.

At each *p*H level in the range of 5 to 9 inclusive, there are only small changes in half-wave potentials with variations in any of the experimental conditions. At *p*H 6 there is little if any difference in half-wave potentials when either potassium hydrogen phthalate or potassium dihydrogen phosphate serves as the principal buffer component since a 0.050 *M* potassium hydrogen phthalate solution having an ionic strength of 0.140 *M* gives a half-wave potential of −0.622 v. In addition to the phosphate system at *p*H 8 the concentration of boric acid was varied from 0.050 to 0.400 *M* and the ionic strength ranged from 0.050 to 0.600 *M*. For the phosphate buffers at the same *p*H the concentration of potassium dihydrogen phosphate was varied from 0.050 to 0.300 *M* with accompanying variations in ionic strengths ranging from 0.144 to 1.014 *M*.

In studies conducted at *p*H 10 when the concentration of potassium dihydrogen phosphate is 0.050 *M*, increasing the ionic strength from 0.153 to 0.600 *M* renders the half-wave potential less negative by 0.018 v. Increasing the concentration of potassium dihydrogen phosphate to 0.320 *M* as the ionic strength is kept at 0.600 *M* and then increasing the ionic strength to 1.015 *M* have no further effect on the half-wave potentials.

Half-wave potentials are independent of con-

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[8] With one exception, potassium chloride was employed in effecting increases in ionic strength in addition to the contribution made by buffer constituents. At *p*H 3 sodium chloride was used with sodium hydrogen tartrate buffer.

[9] In these discussions *p*H values are expressed as the nearest whole number to clarify the exposition. Precise values are given in Table I.

TABLE I

POLAROGRAPHIC BEHAVIOR OF QUINOXALINE IN THE *p*H RANGE OF 1 TO 10

| Buffer[a] | Concn., mmoles/l. | Electrolyte[b] | *p*H | Ionic strength | $E_{0.5}$ (S.C.E.) | | $I_d/Cm^{2/3}t^{1/6}$ | |
|---|---|---|---|---|---|---|---|---|
| | | | | | 1st wave | 2nd wave | 1st wave | 2nd wave |
| H | 0.449 | 0.400 *M* $KHSO_4$ | 0.96 | 0.620 | −0.254 | −0.809 | 3.50 | 2.18 |
| L | .446 | .104 *N* HCl + 0.050 *N* KCl | 1.00 | .154 | − .279 | − .772 | 3.78 | 0.81 |
| H | .449 | .220 *M* $KHSO_4$ + 0.009 *N* KCl | 2.05 | .598 | − .339 | − .889 | 3.37 | .90 |
| L | .446 | .013 *N* HCl + 0.050 *N* KCl | 1.93 | .063 | − .342 | − .865 | 3.82 | .65 |
| H | .449 | .400 *M* NaHTr + 0.200 *N* NaCl | 3.00 | .601 | − .401 | − .936 | 3.24 | 1.13 |
| L | .446 | .050 *M* KHPh | 2.92 | .051 | − .441 | − .935 | 3.71 | 1.42 |
| H | .446 | .400 *M* KHPh + 0.200 *N* KCl | 3.99 | .647 | − .481 | − .981 | 2.90 | 1.20 |
| L | .446 | .050 *M* KHPh | 4.00 | .050 | − .488 | −1.011 | 3.63 | 1.28 |
| H | .449 | .285 *M* KHPh | 4.99 | .598 | − .550 | −1.044 | 3.22 | 0.93 |
| L | .446 | .050 *M* KHPh | 4.99 | .098 | − .554 | −1.053 | 3.64 | .70 |
| H | .448 | .350 *M* $KH_2PO_4$ + 0.086 *N* KCl | 6.00 | .600 | − .617 | −1.092 | 3.46 | .43 |
| L | .447 | .050 *M* $KH_2PO_4$ | 6.00 | .062 | − .616 | −1.06[c] | 3.54 | .14 |
| H | .448 | .260 *M* $KH_2PO_4$ | 6.96 | .606 | − .675 | −1.14[c] | 3.36 | .14 |
| L | .447 | .050 *M* $KH_2PO_4$ | 7.00 | .110 | − .676 | | 3.69 | |
| H | .449 | .200 *M* $KH_2PO_4$ + 0.020 *N* KCl | 7.98 | .600 | − .738 | | 3.23 | |
| L | .447 | .050 *M* $KH_2PO_4$ | 8.00 | .144 | − .745 | | 3.71 | |
| H | .449 | .440 *M* $H_3BO_3$ + 0.456 *N* KCl | 8.62 | .602 | − .777 | | 3.16 | |
| L | .446 | .050 *M* $H_3BO_3$ + 0.050 *N* KCl | 9.00 | .071 | − .798 | | 3.77 | |
| H | .448 | .180 *M* $KH_2PO_4$ + 0.038 *N* KCl | 10.13 | .600 | − .863 | | 3.55 | |

[a] L "Low" buffer; H "High" buffer. [b] Adjusted to final *p*H with sodium hydroxide or hydrochloric acid solution. Ph = phthalate, Tr = tartrate. [c] Too low to be measured more accurately.

centration in the *p*H range of 2 to 9. Variations of 5% are observed at *p*H 1 where differentiation into minor waves is more extensive.

The diffusion current constants for the first major waves have the same order of magnitude throughout the *p*H range of 1 to 10. However, their values tend to decrease with increasing buffer concentration and to a lesser extent with increasing ionic strength. Variations of quinoxaline concentration in both buffer systems give diffusion current constants having deviations of 2 to 8%.

B. **Second Major Wave.**—The trends are different than for the first major wave. At *p*H 1 the half-wave potential varies from −0.772 to −0.803 v. as the ionic strength of the "Low" buffer is increased to 0.617 *M* by addition of potassium chloride. Increasing the concentration of potassium hydrogen sulfate to 0.800 *M* and ionic strength to 1.434 *M* gives the same half-wave potential as found with the "High" buffer. At *p*H 2, the half-wave potentials become more negative with increasing ionic strength and buffer concentration. At *p*H 3, the half-wave potential remains essentially constant as the ionic strength in the "Low" buffer is increased to 0.606 *M* by addition of potassium chloride. Also, the change to the sodium hydrogen tartrate buffer does not affect the half-wave potential as the concentration of this salt is raised to 0.400 *M* and the ionic strength is increased to 0.601 *M*. At *p*H 4 the half-wave potential varies uniformly from −1.011 v. in the "Low" buffer to −0.982 v. in a buffer of 0.250 *M* potassium hydrogen phthalate and potassium chloride having an ionic strength of 0.368 *M*. Further increases in concentration of potassium hydrogen phthalate to 0.450 *M* and the ionic strength to 0.647 *M* do not affect half-wave potentials. At low *p*H the wave is too small to be evaluated accurately in the "Low" buffer. Increasing the buffer concentration to 0.350 *M* potassium dihydrogen phosphate affords a sufficiently high wave for quantitative evaluation. The half-wave potential varies uniformly from −1.079 to −1.101 v. as the concentration of potassium dihydrogen phosphate is increased from 0.350 to 0.600 *M*, and the ionic strength is increased from 0.600 to 1.000 *M* with potassium chloride.

Contrary to the trend noted for the first major wave, the half-wave potentials for the second major wave generally become more negative as the concentration of quinoxaline is increased in the "Low" and "High" buffers. Exceptions are noted at *p*H 1 in the two buffers, *p*H 2 in the "Low" buffer, *p*H 4 in the "High" buffer and possibly at *p*H 6 in the "Low" buffer. In these cases the trends are not uniform and in nearly each instance the size and form of these waves make their evaluations somewhat uncertain. In all cases polarograms were run at quinoxaline concentrations of $2.5 \times 10^{-4}$ *M*, $4.5 \times 10^{-4}$ *M* and $7.0 \times 10^{-4}$ *M*.

The diffusion current constant for the second major wave generally appears to increase with increasing concentration of buffer components, with the influence of ionic strength not being too significant. At *p*H 3, the diffusion current constant is higher in the potassium hydrogen phthalate buffer than in the sodium hydrogen tartrate buffer. In the latter, the diffusion current constant fails to increase with buffer concentration. At *p*H 4 there are no significant increases in diffusion current constants with increasing buffer concentration.

In Fig. 1 is shown the variation in diffusion current constants with *p*H for the second major wave of $4.5 \times 10^{-4}$ *M* solutions of quinoxaline in both systems of buffers. The heights of these waves are not only dependent upon *p*H but also upon buffer composition, as already noted.

The diffusion current constants for the second major wave tend to decrease with increasing concentration of quinoxaline both in the "Low" and "High" buffers. Furthermore, these values tend to have average deviations > ±5% in each buffer system at every *p*H level. It is evident that the

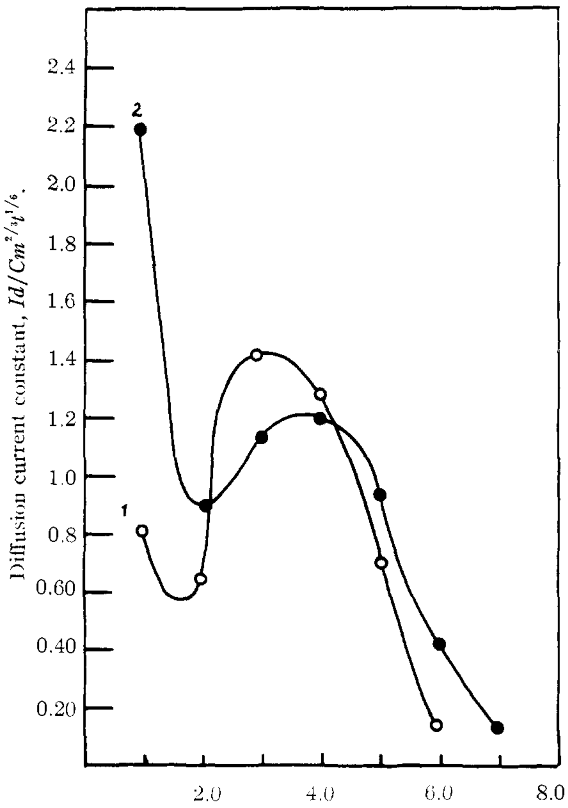


Fig. 1.—Diffusion current constants *vs.* $p$H for $4.5 \times 10^{-4}$ $M$ quinoxaline: 1, Clark and Lubs ("Low") buffers; 2, "High" buffers.

two major waves for quinoxaline represent decidedly different reduction processes.

## Evaluation of $n$ and Discussions

**A. First Major Wave.**—The significant aspects of this wave are (1) diffusion current constants have the same order of magnitude throughout the range of $p$H explored, indicating the same number of electrons involved in reduction, (2) diffusion current constants decrease somewhat with increasing buffer concentration and ionic strength at each $p$H, (3) except for the cases noted at $p$H 1 and $p$H 2, half-wave potentials are independent of the concentration of quinoxaline and (4) with certain exceptions noted at $p$H's 1, 2, 3 and 10 the half-wave potentials are independent of the nature of buffer components, concentration and ionic strength.

Efforts were made to evaluate $n$ of this wave for $4.5 \times 10^{-4}$ $M$ quinoxaline solutions in the "Low" and "High" buffers by means of the Ilkovic equation

$$n = id/605D^{1/2}Cm^{2/3}t^{1/6} \qquad (2)$$

A value for $D$ in the above equation was calculated from the Stokes–Einstein equation where the molar volume of 6-methylquinoxaline was employed. The density for 6-methylquinoxaline of 1.1125 at 25°, reported by Cavagnol and Wilson[10] was used to calculate the molar volume. The value of $D$ obtained by this method is $6.55 \times 10^{-6}$ cm.$^2$ sec.$^{-1}$ at 25°. For $4.5 \times 10^{-4}$ $M$ solutions of quinoxaline in the "Low" buffers and in the "High" buffers the values of $n$ varied from 1.9 to 2.5 with the average being 2.3.

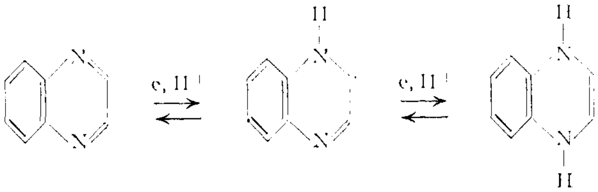
It is evident that the first major wave represents reduction involving two electrons. At $p$H's 1 and 2 wave differentiation into two equal portions signifies that reduction may proceed as a bimolecular reaction in two successive one-electron steps. It has been observed in our laboratory that the quinoxalinium ion behaves as a strong acid which makes it unlikely that the conjugate acid is being reduced. This condition may exist at $p$H 3 in the "Low" buffer but as an increase in buffer concentration appears to remove evidence of such differentiation completely then the wave differentiation may have been due to inadequate buffering. At higher $p$H's, reduction must proceed by the simultaneous addition of two electrons.

The equation of a reversible electrode process for an inorganic substance involving the addition of $n$ electrons and $n$ protons in a buffered solution indicates that the variation of half-wave potential with $p$H should be linear with the slope being $-0.059$. The plot of half-wave potential *versus* $p$H for $4.5 \times 10^{-4}$ $M$ solutions of quinoxaline in the "Low" buffers gives a straight line from $p$H 1 to $p$H 5 having a slope of 0.070. A straight line can be drawn from $p$H 4 to $p$H 9 having a slope of 0.063.

A similar plot for $4.5 \times 10^{-4}$ solutions of quinoxaline in the "High" buffers gives a straight line from $p$H 1 to $p$H 10 having a slope of 0.063. Evidently, similar orders of reversibility are prevalent in the "Low" buffers and the "High" buffers. Reduction occurring at the low $p$H's is not as reversible as the reduction occurring at higher $p$H's.

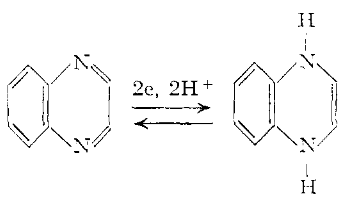
On the basis of the analysis of results for the first major wave, the following mechanisms are proposed.

In the $p$H range of 1 to 2 inclusive, dihydroquinoxaline is formed by two consecutive single-electron steps



I III IV (3)

At $p$H's > 4 reduction follows the simultaneous two-electron process



I IV (4)

At $p$H 3 reduction may proceed by either of the above processes.

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(10) J. C. Cavagnol and G. Wilson, Jr., THIS JOURNAL, **72**, 3752 (1950).

It is postulated that 1,4-addition occurs in preference to 1,2-addition owing to the greater electronegativity of nitrogen. Also, it has been found in the polarographic reduction of other simple nitrogen-containing systems such as quinoline[11-13] and acridine[14] that reduction to the *dihydro* stage occurs at the 1,4-position.

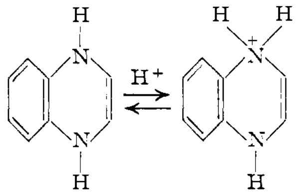
The tendency for nitrogen-containing heterocyclic systems to undergo reduction to the *dihydro* form by a semiquinone process in acid media and by a simultaneous two-electron process in alkaline media has been observed for 2-carboxyquinoline,[11] 8-carboxyquinoline,[12] 4-carboxyquinoline,[13] and methylpyridinium hydroxide.[15]

**B. Second Major Wave.**—The significant aspects of this wave are (1) it is present in acidic media but vanishes at *p*H's > 7, (2) the height increases with increasing concentration of acidic buffer component but not necessarily increasing ionic strength, except at *p*H 3 and *p*H 4. At *p*H 3 and *p*H 4 the diffusion current constants appear to be independent of concentration of potassium hydrogen phthalate and of ionic strength, (3) the variations in the diffusion current constants with quinoxaline concentration at each *p*H are greater than those of the first major wave. This suggests that the second major wave does not strictly follow the Ilkovic equation relating diffusion current and reductant concentration, (4) the half-wave potentials become more negative with increasing concentration of quinoxaline except for the results found in the "Low" buffers at *p*H 1, 2 and 6 where there are no uniform trends, (5) the half-wave potentials of this wave generally appear to be more sensitive to variations in buffer components, buffer concentration and ionic strength than those for the first major wave.

Kolthoff and Lingane[16] gave the relation describing the change of half-wave potential with change in acid concentration due to hydrogen discharge for a weak acid in an excess of indifferent supporting electrolyte as

$$\Delta E_{0.5}/\Delta \log [\mathrm{HA}] \simeq -0.089 \text{ v.} \qquad (5)$$

where HA represents the weak acid. By taking $\Delta E_{0.5}/\Delta \log [\mathrm{HA}]$ quotients from the results obtained in this investigation for the variation in half-wave potentials of the second major wave with quinoxaline concentration, an average value of $-0.083$ v. is obtained for quinoxaline in both buffers. On this basis it is postulated that the second major wave is hydrogen reduction catalyzed by the 1,4-dihydroquinoxalinium ion (V), *viz.*



IV V

(6)

It is believed that the catalytic action is caused by the dissociation of V which is presumed to be a weak acid. According to Cavagnol and Wilson,[10] the first and second acid dissociation constants of 1,2,3,4-tetrahydroquinoxaline are $7.8 \times 10^{-3}$ and $1.45 \times 10^{-5}$, respectively. Electronic considerations dictate that 1,2,3,4-tetrahydroquinoxaline is a weaker acid than 1,4-dihydroquinoxaline. Thus the proton leading to the catalytic wave comes from the monobasic acid.

The conclusion that the second major wave is due to hydrogen discharge catalyzed by the *dihydro* form of quinoxaline, is not unique for heterocyclic systems. Knobloch[17] observed that the reduction of nicotinamide proceeded to the dihydro stage which catalyzed the evolution of hydrogen in acid and neutral media. Catalytic hydrogen waves have been reported to follow the reduction of quinoline in weakly acidic media.[18] Kirkpatrick[19] found catalytic hydrogen waves for a number of alkaloids containing the indole structure as well as for quinine and quinidine. The failure to obtain tetrahydroquinoxaline in aqueous media at *p*H's > 7 where kinetic waves are absent must be due to the existence of the isolated double bond in the 2,3-position. Compounds containing a single ethylenic function are not ordinarily reduced at the dropping mercury electrode.[20]

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MADISON, NEW JERSEY

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