# POLAROGRAPHY OF HETEROCYCLIC COMPOUNDS

## I. MISCELLANEOUS DATA ON THE POLAROGRAPHIC BEHAVIOR OF HETEROCYCLES AND ELECTROCHEMICAL REDUCTION OF HETEROAROMATIC COMPOUNDS (REVIEW)

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Polarography (voltamperometry) – microelectrolysis on a dropping mercury electrode (DME) [1-12] – is an established technique in the modern complex of physicochemical methods for the study of organic compounds. This method, which was proposed in 1922 by J. Heyrovsky, continues to remain extremely effective and even indispensable in the solution of a number of scientific problems of organic chemistry, for example: to find the standard redox potentials of organic redox systems or values close to those potentials that include a certain kinetic component – the polarographic half-wave potentials ($E_{1/2}$); to ascertain the nature and sequence of steps of a complex electrochemical reduction reaction [11, 13], which often proceeds in a manner similar to reactions of chemical, catalytic, and biochemical reduction; to find the approximate values of the diffusion coefficients of organic molecules; to select the conditions for the electrochemical synthesis of organic compounds; to select the conditions for the electrochemical generation of free ion radicals, the study of which subsequently by ESR spectroscopy gives unique information regarding the distribution of the unpaired spin in the particle [14]; to find characteristics of the energy of the lower vacant and, in the case of oxidative voltamperometry, the higher occupied molecular orbital, the magnitude of which in a series of related compounds follows the trend of the experimental $E_{1/2}$ values; for the analytical determination of milli- and microconcentrations of organic substances.

In addition, polarography makes it possible to solve a multitude of specific problems in the electrochemistry of organic compounds, such as the determination of the rate constants for electron transfer, determination of the rate constant of an ultrahigh-speed protonation reaction, determination of the adsorption characteristics of organic molecules on the charged surface of an electrode, investigation of the effects of the electrical double layer, etc.

The peculiarities of the polarographic reduction of heterocyclic systems were considered in reviews by Volke [7, 15, 16] and Elving [17, 18], and two reviews by Lund devoted to the examination of the electrochemical transformations of heterocyclic compounds in general [19] and nitrogen-containing heterocycles in particular [20] recently appeared.

However, the reviews mentioned above do not completely encompass the newest material and inadequately reflect the research done in the USSR. We therefore deemed it expedient to address ourselves to this problem. The aim of the present review is a systematic examination of the polarographic behavior of fundamental types of heterocyclic compounds and the presentation of some principles by which the research organic chemist who desires to use this method for the study or analysis of heterocyclic compounds and natural and biologically active substances of heterocyclic structure might be guided.

In the first part of this review only those systems in which either the heteroring itself or a system containing both the heteroring and the substituent in conjugation with it is reduced are examined.

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## 1. General Aspects

The most useful classification in the systematization of data on the polarographic behavior of the numerous and diverse heterocyclic systems is that proposed by Albert [21], according to which the heterorings are subdivided into heteroparaffin, heteroethylenic, and heteroaromatic compounds.

Heteroparaffin (i.e., completely saturated) heterocyclic compounds generally are not reduced on a DME – their activity may be due only to cleavage of the strongly polarized single bonds of the heteroring, the catalytic effect of the heterocycle on the electrochemical liberation of hydrogen, or reduction of the electroactive functional groups of the side chain. In a number of cases, heteroethylenic compounds (i.e., unsaturated but not completely conjugated systems that are devoid of aromaticity) are endowed with polarographic activity and behave like acyclic $\alpha,\beta$-unsaturated functional derivatives.

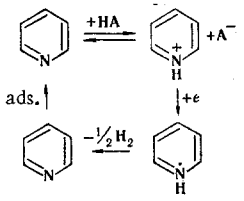
The greatest number of electroactive compounds that are capable of reduction on a DME are those in the heteroaromatic-compound class (i.e., completely unsaturated cyclic compounds that have an aromatic sextet of $\pi$ electrons and the corresponding annelated systems).

Heteroaromatic compounds can be subdivided into $\pi$-deficient and $\pi$-surplus heteroaromatic systems. Of these, the former are polarographically active, since, because of the deficiency of $\pi$ electrons in any position of the ring, the molecules undergo nucleophilic attack by an electron (i.e., the primary act of electrochemical reduction) more readily than benzene and the corresponding aromatic hydrocarbons. Moreover, the heteroatom in compounds of this type is capable of being protonated, alkylated, etc., thereby acquiring a positive charge; this substantially facilitates electrochemical reduction. Polarographically active heterocycles of this type are six-membered nitrogen-containing heterocycles of the pyridine, quinoline, pyrimidine, etc. type. The $\pi$-surplus heterocycles include nitrogen-, sulfur-, and oxygen-containing heterocycles (primarily the five-membered compounds) in which the unshared pair of electrons of the heteroatom participates in the $\pi$-electron sextet and is responsible for the excess of $\pi$ electrons in any other position of the cyclic system (for example, pyrrole, furan, thiophene, indole, carbazole, etc.); these heterocycles are not reduced on a DME and are not inclined to undergo protonation. The $\pi$-surplus effect predominates in the case of five-membered heteroaromatic systems with several heteroatoms that simultaneously contain both "pyridine" and "pyrrole" nitrogen atoms (or an oxygen atom or sulfur atom, respectively), and the system does not have the ability to undergo polarographic reduction (pyrazole, imidazole, oxazole, thiazole, etc.).

The increased ability of heteroaromatic systems (or the products of their electrochemical conversion) to be adsorbed on the surface of a mercury electrode takes on a more significant role during the electroreduction of heteroaromatic systems than during the electroreduction of aromatic systems, and this frequently changes their polarographic behavior substantially as compared with the analogs of the benzene series. A factor of no less importance is the ability of nitrogen-containing (and sometimes oxygen- and sulfur-containing) heterocycles to undergo protonation in the unadsorbed or adsorbed states. On the one hand, the acquisition of positive charge may facilitate electroreduction of the heteroring, but more often the possibility of protonation leads to the formation of a catalytic hydrogen wave; this is a characteristic peculiarity of the polarographic behavior of nitrogen-containing heterocycles [3].

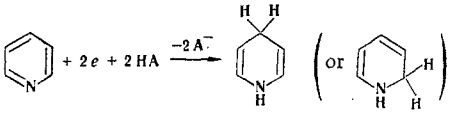
## 2. Heteroaromatic Systems in Which the Heteroring Itself Is Reduced. Compounds with One Heteroatom

Pyridine and Its Derivatives. Although much research has been devoted to the polarographic behavior of pyridine and its simplest derivatives, there is not complete clarity regarding the mechanism of the electroreduction of this system as a function of the medium [22-32]. In aqueous media pyridine gives the catalytic wave of the liberation of hydrogen [24, 27]. The peculiarities of this wave and the effect on it of the most diverse factors [3, 32-38] have been the subject of independent investigations. The electrochemical process responsible for the appearance of the catalytic wave [24] consists of a set of reactions, the end result of which is liberation of hydrogen from the molecules of a protogenic solvent, for example, water:



The opinions with regard to whether pyridine in aqueous solutions is also capable of giving a wave for the reduction of the pyridine ring itself in addition to the hydrogen catalytic wave are contradictory. Some authors suppose that pyridine gives a reduction wave at −1.5 to −1.8 V, in which case the electrochemical process results in the two-electron reduction of pyridine to dihydropyridine [22]. The peak on the oscillograms at −1.7 V in a Britton−Robinson buffer solution with pH 7.5 is due to discharge of hydrogen ions. However, the mechanism of the electrochemical transformation of pyridine is complicated in oscillopolarography; dipyridyls (which indicate parallel dimerization of radicals) and even oxygen-containing heterocycles and glutaconic aldehyde are detected in the electrolysis products [30, 31].

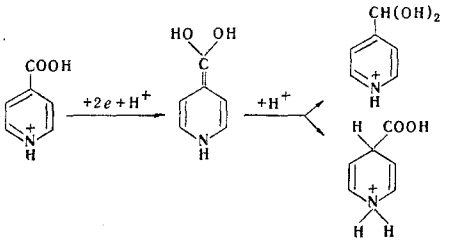
It seems probable that under the conditions of classical polarography in aqueous media pyridine in the protonated form primarily only catalyzes the liberation of hydrogen ions (in this case the dipyridyls that are formed during the electrolysis because of dimerization of the intermediate free radicals are also catalysts in addition to pyridine [35]) but is not reduced at all in the unprotonated form. In dimethylformamide (DMF), however, the unprotonated form of pyridine gives a two-electron (2e) wave for the reduction to dihydropyridine at potentials above −2 V [28]:



A one-electron (1e) wave from the reduction of the protonated form of pyridine appears during polarography of pyridinium ions in pyridine (i.e., of various acids in pyridine); the resulting dimers of the free radicals are reduced to tetrahydropyridols. A similar mechanism also occurs in mixed aqueous pyridine media containing up to 10% (by volume) water; however, at water concentrations of 50% (by volume), only catalytic liberation of hydrogen is observed [39].

Pyridine derivatives that contain an electron-accepting but electrochemically inactive substituent attached to the ring are also capable of giving true 2e waves from the electroreduction of the pyridine ring in addition to the catalytic waves. Isonicotinic, picolinic, and nicotinic acids give reduction waves [40-44], and in this case, as the pH increases, the more positive wave of ~ −1.0 V, which corresponds to the dipolar ion, decreases at the expense of an increase in the more negative wave of ~ −1.7 V, which is ascribed to the acid anion. In complete accordance with the order of the change in the electronic substituent effects, the $E_{1/2}$ values are shifted to more negative potentials in the following order: pyridine-4-, pyridine-2-, and pyridine-3-carboxylic acids [44].

The data from preparative electrolysis indicate that only the pyridine ring is involved in the case of nicotinic acid, while the carboxyl group is involved in the case of the two remaining acids, and hydrated $\alpha$- and $\gamma$-formylpyridines are formed [43]. In addition, colored compounds – products of conversion of the dihydropyridinecarboxylic acids – are formed as side products [43].

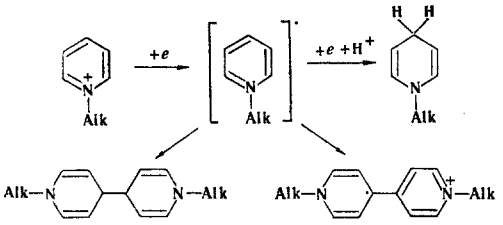


4,4'-Dipyridyl gives two waves, the first of which corresponds to transfer of one electron and leads to the formation of a blue free radical [45]. The isomeric dipyridyls are also reduced in the order 4,4' > 2,2' > 3,3' [46, 47].

2e-Reduction of the pyridine ring in the protonated or unprotonated state is also assumed in the polarographic reduction of diverse substituted cyanopyridines and pyridinecarboxamides [48], although different assumptions relative to the nature of the latter electrochemical processes have also been expressed.

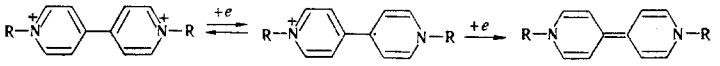
Pyridinium Salts. When the nitrogen atom of the pyridine ring is alkylated, the quaternary nitrogen atom loses its ability to undergo protonation and thereby to form a catalytic hydrogen wave. N-Alkylpyridinium salts give two 1e waves in aqueous solutions; the $E_{1/2}$ value of the first reversible or partially reversible step at −1.0 V is independent of the pH, and the process leads to a free radical, which is par-

tially dimerized in the second step ($E_{1/2}$ depends on the pH) and is partially reduced subsequently (at −1.7 V) to the corresponding N-alkyl-1,2- or -3,4-dihydropyridine [49-52]. The radical formed in the first step is quite stable, but it corresponds to a radical of dimeric structure and apparently is a secondary product:



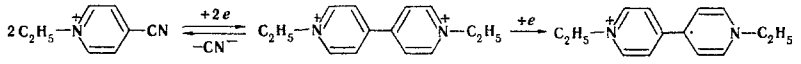
The same mechanism of electrochemical reduction was also established for N-methylnicotinamide and related compounds [51], but in this case reduction proceeds at more positive potentials and involves primarily the 6 position of the ring only if the substituent attached to the nitrogen atom does not create steric hindrance (for example, propyl groups and the like) [18].

The coenzyme nicotinamide-adenine dinucleotide (NAD, DPN, codehydrogenase), which participates in hydrogen transfer in biochemical systems, gives one reduction wave at −0.8 to −1.1 V in both acidic and alkaline media [18, 52-59]. It is assumed that here also 1e reduction leads to a radical that then dimerizes in the 4,4' position [51]. However, the dimer could not be isolated by controlled-potential electrolysis (CPE), and products that have a certain coenzymatic activity (from 0 to 76% of that expected for NAD) were formed; parallel 2e reduction to the corresponding dihydropyridine therefore cannot be excluded. The reverse electrooxidation of reduced form NADH (DPNH) occurs at more positive potentials (from −0.2 to −0.4 V), and, consequently, in contrast to biochemical reactions, a reversible redox pair between NAD and NADH is not formed in the electrochemical experiment. It is possible that the reason for this is retardation of transfer of the second electron by the adsorbed dimers. N,N'-Dialkylpyridinium salts give two 1e waves, the first of which (at −0.7 V) is reversible and has an $E_{1/2}$ value that is independent of the pH [60, 61]. The blue radical cation that is formed is capable of undergoing both further 1e reduction (at −1.1 V) and reversible oxidation, while the final quinoid product rapidly rearranges and therefore does not give an anode wave:

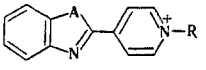


R = $CH_3$, $C_2H_5$, $CH_2C_6H_5$

A similar intermediate dialkyldipyridyl radical also arises during 1e reduction of N-alkylpyridinium salts [49] and also from N-alkyl-4-cyanopyridinium salt after prior electrochemical cleavage of a $CN^-$ ion and subsequent dimerization of the intermediate radical.



The electrochemical reduction of N-substituted benzazolylpyridinium salts [62] proceeds with formation of 1,4-dihydropyridine via a radical mechanism, in which case their electroreduction is facilitated considerably as compared with pyridinium salts that do not contain a benzazolyl substituent.



A = O, S, NH; R = $CH_3$, $CH_2C_6H_5$

The first step in the polarographic reduction of N-substituted pyridinium salts (and apparently in the polarographic reduction of all of the previously considered pyridine derivatives that are reduced in the protonated form) is the formation of a free radical, which then either dimerizes rapidly (with a rate constant of $5 \cdot 10^8$ liter · mole/sec [37]) or is further reduced, depending on the type of compound, conditions of the medium, depolarizer concentration, etc. It should be noted that free radicals in amounts sufficient for recording could not be obtained in the electroreduction of pyridines by electrochemical generation while such radicals are quite stable for dipyridyls, where delocalization of the unpaired electron over the system of conjugated bonds is more likely.

Pyridylethylenes. The isomeric 1,2-dipyridylethylenes are reduced on a DME in two 1e steps or more often in one 2e step to dipyridylethanes, during which the 4,4'-isomer, in contrast to the 2,2'-isomer,

is reduced reversibly in neutral and alkaline media; this indicates the participation of the entire conjugated system in the electrochemical reaction [63]. It has been shown by the use of the Kalousek technique and analysis of the i,t curves that some 4-substituted pyridines and the corresponding pyridinium salts, where the formation of quinoid intermediate forms is conceivable, are reduced reversibly or almost reversibly (they give anode stages at the same potentials as the cathode stages or at potentials 20-30 mV greater than the anode values) [64]. 1,4-Bis[(4-pyridyl)vinyl]benzene, 1,2-di(4-pyridyl)ethylene, 4,4'-dipyridyl, and pyrazine are included in systems of this sort. At the same time, 2,2'-dipyridyl and stilbazole are reduced irreversibly. The mechanism of the transfer of the first and second electrons in the indicated systems was studied in acetonitrile with the gradual addition of water [65], and, in addition, inhibition of the electrode process because of adsorption of an electroactive substance was investigated [66].

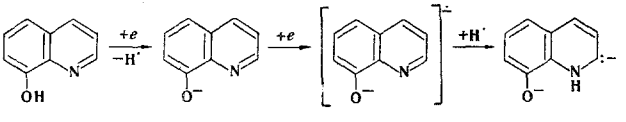
Polynuclear Systems with a Pyridine Ring. Annelation of the pyridine ring considerably facilitates the electroreduction of the molecule: while pyridine itself is reduced at −2.07 V in dimethylformamide (5% water), under the same conditions isoquinoline is reduced at −1.84 V, and quinoline, benzoisoquinoline, benzoquinoline, phenanthridine, and acridine, respectively, are reduced at −1.69 V, −1.78 V, −1.70 V, −1.64 V, and −1.24 V. This order of electroreduction corresponds to the change in energies of the lower vacant MO calculated for these heterocycles (however, the $E_{1/2}$ value of pyridine deviates from the linear correlation) [67, 68]:

$$E_{1/2} = -0.555 + 2.127 m_{n+1}^{(N)}, \; r = 0.986.$$

The indicated dependence remains in force also for monoazaheterocycles with four and five benzene rings in the molecule [68], but it is of approximate character, since not all of the monoazaheterocycles are reduced via the same mechanism.

In contrast to pyridine derivatives, 2e waves are often observed for annelated monoazaheterocycles in proton-donor media; this is apparently explained by the lower rate of dimerization of the intermediate free radicals, but subsequent 1e reduction steps are also observed for them in aprotic media. In the general case, depending on the structure and medium, polynuclear monoazaheterocycles may give 1e and 2e waves and a wave of intermediate height. In addition, catalytic hydrogen waves that usually follow the reduction waves or merge with them are also formed as a rule.

Quinoline and Its Derivatives. In aqueous neutral, weakly alkaline, and aqueous organic media, quinoline and its derivatives are reduced to 1,2- or 1,4-dihydroquinolines in the accessible range of potentials (from −1.4 to −1.6 V) with the consumption of two electrons [69-72]. The catalytic liberation of hydrogen is superimposed on this wave in acidic media. Quinoline in 100% DMF gives two successive 1e steps at −2.0 to −2.6 V [73]. 8-Hydroxyquinoline (oxine) in acidic media gives one 2e wave at $E_{1/2}$ from −0.85 to −1.5 V, the height of which decreases to the 1e level as the pH increases [74, 75]. In DMF, 8-hydroxyquinoline is reduced in two 1e steps (at −1.82 and −2.5 V), and the first wave corresponds to discharge of the hydrogen of the hydroxyl group, while the second corresponds to one-electron reduction of the pyridine ring to the quinolinolate anion, which reacts rapidly with the atomic hydrogen formed in the first step to give the 1,2-(or 1,4-)dihydroquinolinolate anion:



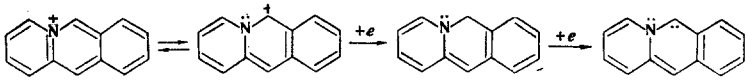
The electroreduction of 5-hydroxyquinoline proceeds similarly [76, 77]. Quinolinecarboxylic acids are reduced in the same way as pyridinecarboxylic acids [78]. The ability of the quinoline ring to undergo polarographic reduction was used to develop methods for the analytical determination of biologically important substances, for example, quinine, and cinchophen (atophan) [79].

It should be noted that quinoline derivatives under well-known conditions give catalytic and adsorption waves, and it is therefore recommended that they be studied in mixed aqueous organic or organic media. This is true to an even greater degree for acridine and its derivatives [80-83]. The electroreduction of acridine proceeds in two irreversible 1e steps to give an intermediate free radical and then acridan, and the electrolysis products have extremely high adsorbability on a mercury electrode; this frequently causes complications on the polarograms. The polarographic method has been used for the study and analysis of numerous acridine derivatives that have biological activity (see [79] and [84, 85]).

Isoquinoline. Isoquinoline, like quinoline, in neutral Britton–Robinson buffer solutions gives a 2e wave, which decreases as the pH rises and disappears completely when pH > 10 [72]. In acidic media, this wave is overlapped by the wave from catalytic liberation of hydrogen.

Alkylquinolinium and Alkylisoquinolinium Salts. These salts give, over the entire pH interval, distinct polarographic waves due to reversible transfer of one electron with subsequent dimerization of the resulting radicals [72, 86, 87]. The waves of the salts appear at substantially higher positive potentials (−0.90 V and −1.27 V) than the waves of quinoline and isoquinoline (−1.27 V and −1.24 V, respectively). Indole is not reduced on a DME, indolenine gives a wave at −1.54 V, while indoleninium salts give a wave at −1.36 V [88].

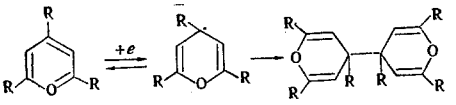
The acridizinium ion in acidic media gives two 1e waves at −0.8 and −1.0 V, respectively, the first of which is reversible [89]:



The absence of a dependence of the reduction potentials of both steps on the pH indicates that a hydrogen ion is not included directly in the electrode reaction. However, the carbanion formed reacts rapidly with protons from the protolytic medium.

A wave from the product of hydrolytic cleavage of acridizinium ions appears in alkaline media.

Pyrylium and Thiapyrylium Salts. 2,4,6-Substituted pyrylium and isobenzopyrylium salts, which give a reversible 1e wave at −0.5 to −0.9 V [66, 90-93], are also reduced in the same way as pyridinium salts. The CPE data provide evidence that the primary radicals dimerize to substituted dipyrans:



Thiapyrylium salts also have polarographic activity [94].

## Compounds with Several Identical Heteroatoms

This category contains primarily six-membered diazines, and some of these systems with a symmetrical structure are reduced reversibly in protogenic media with the loss of two electrons, as in the case of quinones (pyrazine, quinoxaline, and phenazine), while others are reduced irreversibly. Here also, in aprotic media the Hoijtink steps are initially realized in one or another sequence, i.e., there is alternate transfer of two electrons with subsequent protonation of the anion radical and dianion, in the course of which a product that is reduced more readily than the starting depolarizer (and, consequently, the formation of a 2e wave) may be formed [95, 96]. Here also, therefore, one cannot propose a reduction scheme specific for a given heterocycle, as everything depends on the experimental conditions.

The $E_{1/2}$ values of diazines in acetonitrile fit on one correlation line that links the set of $E_{1/2}$ values with the calculated energies of the lower vacant MO [95-97]. Because of differences in the solvation of the derivatives of the two series, this line does not coincide with the analogous line for monoazines but proceeds almost parallel to it:

$$E_{1/2} = -0.84 + 2.42m_{n+1} \text{ (V) (for monoazaheterocycles),}$$

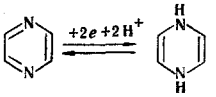
$$E_{1/2} = -0.78 + 2.09m_{n+1} \text{ (V) (for diazaheterocycles).}$$

In addition, a separate line for monocyclic derivatives (pyridine, pyrimidine, pyridazine, and pyrazine) can be constructed from the equation

$$E_{1/2} = 0.19 + 3.70m_{n+1} \text{ (V).}$$

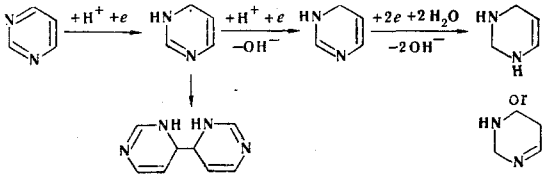
The rate constants for electron transfer calculated from the Koutecky formula also indicate an approximately similar trend.

Pyrazine. Pyrazine is reduced reversibly in protogenic media (Britton–Robinson buffer solutions) at low cathode potentials (~ −0.7 V) with respect to the overall reaction [98-100] to give one 2e wave:

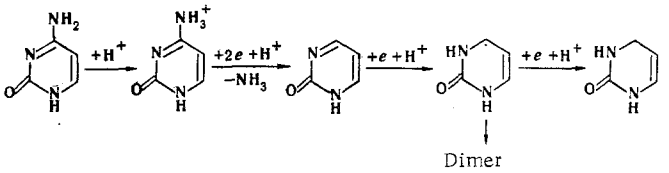


When methyl groups are introduced into the pyrazine molecule, the electrochemical process becomes irreversible. In addition, catalytic hydrogen waves are observed at higher potentials.

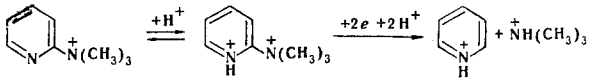
Pyrimidine and Its Derivatives. The polarographic behavior of pyrimidines was investigated in quite some detail by polarography, coulometry, preparative macroelectrolysis, and a spectrophotometric study of the reaction products [101-107]. In protogenic media, the pyrimidine ring is reduced irreversibly and at substantially higher potentials than the pyrazine ring (above −1.0 V). In acidic media, (pH < 5) there is initially 1e reduction to the free radical, which either dimerizes or is reduced at higher potentials to 3,4-dihydropyrimidine; the latter can be further reduced to tetrahydropyrimidine. At pH > 5, the first and second waves merge into one 2e wave, while all of the waves merge into one 4e wave at pH > 9 [101]:



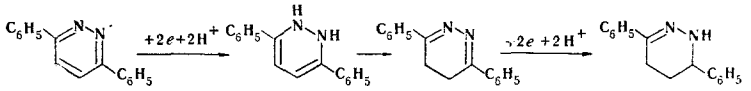
Cytosine (4-amino-2-hydroxypyrimidine) gives a 3e (and, in some cases, a 4e) polarographic wave due to the overall process of electrochemical 2e-deamination and one-electron reduction of the resulting 2-hydroxypyrimidine to a free radical, which either dimerizes or is further reduced to 2-hydroxy-3,4-dihydropyrimidine [101, 108].



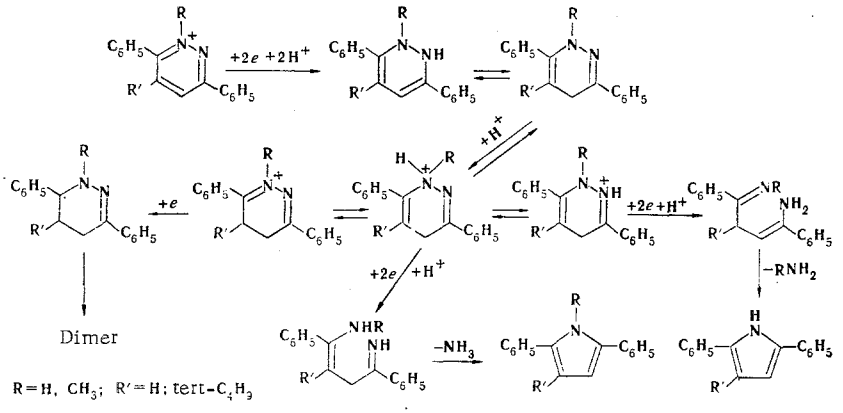
A similar cleavage of a protonated amino group also occurs in the polarographic reduction of 2-pyridyltrimethylammonium iodide [109].



Pyridazines. Pyridazines undergo polarographic reduction in a still more complex manner. While reduction of 3,6-diphenylpyridazine in alkaline media proceeds in two steps to the tetrahydro derivative via the scheme [109, 110]

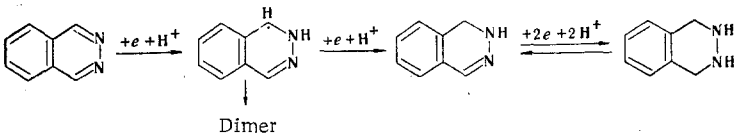


when two substituents are present or in the case of alkylated pyridazinium salts, the second step of the reduction is accompanied by ring contraction leading to pyrrole derivatives, which were identified on the basis of the NMR spectra after CPE [109].



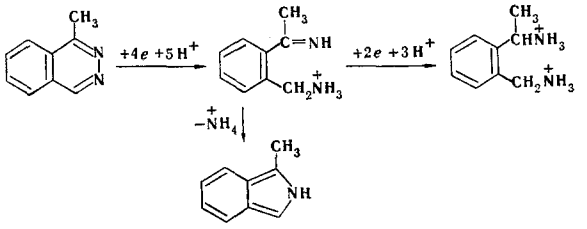
Quinoxalines. Quinoxalines are reduced in aqueous organic media at pH < 4 in two one-electron steps (at −0.2 to −0.5 V and from −0.8 to −1.0 V, respectively), and they then give one 2e wave ($E_{1/2} = -1.1$ V) at pH 4-10 [111-116]. Controlled-potential electrolysis showed that the reaction products are 1,4- and 1,2-dihydro derivatives (and 3,4-dihydro derivatives in the case of substituted quinoxalines) [115]. The individual steps of this process were examined in detail in [115].

Phthalazines and Cinnolines. In contrast to quinoxaline, phthalazine is reduced irreversibly. In alkaline media, phthalazine is reduced via the scheme [109]



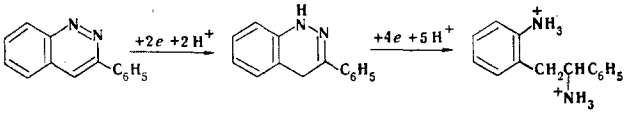

The amount of dimer decreases as the voltage increases, and oxidation of 1,2,3,4-tetrahydrophthalazine to 1,2-dihydrophthalazine [117] may occur when the voltage decreases (at −0.2 V).

However, in acidic media the reaction proceeds further with ring cleavage, in an overall 6e wave, to o-(aminomethyl)benzylamine [118]. A 4e wave is formed in the case of 1-methylphthalazine (at −0.75 V), and this 4e wave is followed by a 2e wave. 1-Methylisoindole may be formed as a result of electroreduction at the potentials of the first wave [109]:

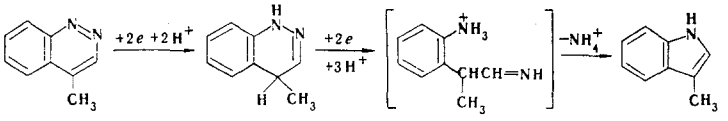



On the whole, however, the electrochemical reduction of phthalazine and its derivatives proceeds in a more complex manner with numerous intermediate steps and side products [119].

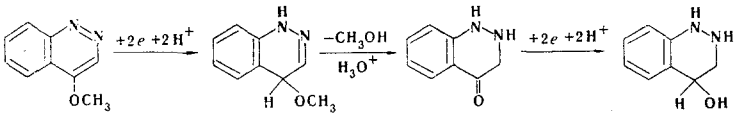
The same cleavage of the N−N bond is also observed in the course of the electroreduction of 3-phenylcinnolines [120]. The reduction proceeds in two steps at −0.5 and −1.2 V, respectively:




In the case of 4-alkylcinnolines, in which the intermediate azomethine derivative is reduced with greater difficulty, ring closing (at −1.0 V) is observed after the first step of the electroreduction (at −0.4 V) [120]:



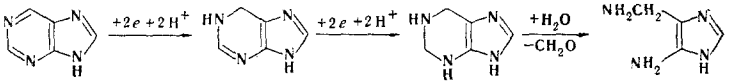

One 2e wave (at −0.5 V) is observed as a result of the electroreduction of 4-methoxycinnoline, and a second wave corresponding to reduction of the 1,4-dihydrocinnoline formed during catalytic demethoxylation appears only in strongly acidic media (at −1.2 V) [120]:




Phenazine. The electrochemical reduction of phenazine in nonaqueous media proceeds in two 1e steps through the intermediate formation of an anion radical, for which the ESR spectrum can be recorded [121, 122]. A radical cation, which can also be obtained by electrooxidation of 9,10-dihydrophenazine [121], is formed in the electroreduction of the diprotonated phenazine cation.

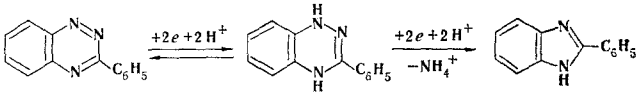
Pteridines. Diverse pteridines also undergo electrochemical reduction at the C=N bond, and it is assumed that the reduction proceeds in the pyrazine ring (the 7,8 position) [116, 123]. A review of the polarography of pteridines, including folic acid, is given in [124, 125].

Purine and Its Derivatives. The polarographic behavior of purine and its derivatives in aqueous media has been studied systematically. At low pH values purine gives two 2e waves, but any polarographic waves vanish at pH > 6, from which it follows that purine is reduced only in the protonated form. According to Elving [17, 18, 102, 105, 126], the first wave (at −0.7 V) is due to saturation of the C=N bond in the 1,6 position, while the second wave (at −0.9 V) is due to further reduction of the resulting 1,6-dihydropurine to 1,2,3,6-tetrahydropurine, which is then hydrolyzed to the 4-aminoimidazole derivative:

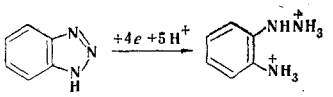


A similar course of electroreduction also occurs in the case of adenine (6-aminopurine), but cleavage of the 6-amino group occurs here in place of the described processes. The cleavage of the 6-amino group is slow and is therefore manifested only in the course of prolonged electrolysis at a controllable potential; it does not have time to be realized during recording of the polarogram; the polarogram of adenine in acidic media contains only one 4e wave, the $E_{1/2}$ value of which depends on the pH, while all waves vanish at pH > 6 [127-129]. The above also pertains to the purine nucleoside adenosine and the corresponding nucleotides, which, like adenine, do undergo reduction, but at somewhat more negative potentials [17, 18, 126].

Triazines. 3-Phenylbenzo-1,2,4-triazine in acidic media gives an almost reversible 2e wave (at −0.1 V), which is followed by an irreversible 2e wave (at −0.95 V) [109]:



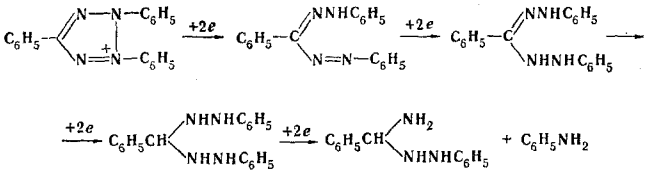
Triazoles. Benzotriazoles undergo reduction in acidic media accompanied by ring opening [109]:



Benzotriazoles are not, as a rule, reduced in alkaline media; only 2-substituted benzotriazoles give a reversible 2e wave:

2,4,5-Triarylimidazoles are oxidized on a DME over an accessible range of potentials, and either dimers of cation radicals (if the aryl group is not capable of quinoidization) or a structure of the quinoid type is formed [130, 131].

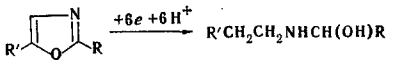
Tetrazolium salts are reduced to formazans on a DME at extremely positive potentials (from −0.1 to −0.5 V), and the reduction in alkaline media proceeds with the overall consumption of eight electrons per molecule. The proposed scheme for the reduction is the following:



One overall 4e wave is observed in acidic media, and benzhydrazine is formed [132-134].

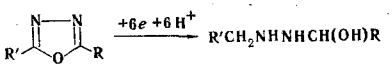
Sulfur-containing heterocycles, for example, 1,2-dithiol-3-thiones, which give two diffusion 2e waves at −0.6 to −1.5 V in 20% aqueous alcohol McElvain buffer solution, also have polarographic activity [135].

Oxazoles and Oxadiazoles. Oxazoles are reduced at −1.9 to −2.1 V with the consumption of six electrons, and the overall wave includes both saturation of the double bonds and opening of the heteroring [136-140]:



If R or R' = $C_6H_5$, $C_{10}H_7$, the process terminates with reduction of the C=N bond and has 2e character.

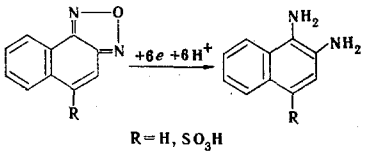
1,3,4-Oxadiazoles are also reduced via a 6e mechanism but at more positive potentials (from −1.8 to −1.9 V) than oxazoles [137]:



Cleavage of the C−O bond does not occur in the case of symmetrical oxadiazoles (R' = R), and the wave has 4e height.

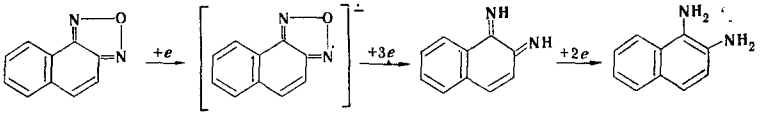
Both types of compounds are reduced with greater difficulty than azomethines of the open series. It follows from the character of their spectra that the electrochemical process does not include cleavage of the C−N and N−N bonds [138].

Aromatic 1,2,5-oxadiazoles (furazans) are reduced in aqueous alcohol solutions at −0.76 to −1.32 V with the formation of one 6e wave [141]:

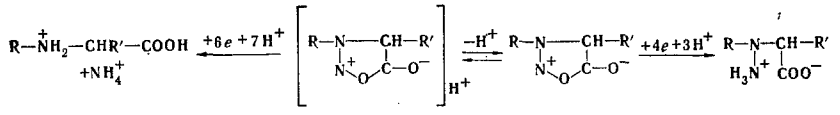


The 6e reduction of 3,4-dihydronaphtho-1,2-furazan-4-sulfonic acid proceeds with greater difficulty than the reduction of nonhydrogenated derivatives. The $E_{1/2}$ values are intermediate between the corresponding potentials for aromatic and aliphatic compounds. This is apparently explained by the fact that hydrogenation of the double bond in the 3,4 position of naphthofurazan leads to considerable disturbance of the $\pi$-electron interaction of the oxadiazole ring with the more distant aromatic ring.

In DMF naphthofurazan is reduced in steps (the $E_{1/2}$ values are, respectively, −1.43, −1.82, and −2.14 V) via the following scheme:



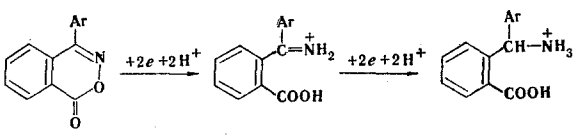
Sydnones. Zuman has shown [142] that the two conjugated forms of sydnones in a Britton−Robinson buffer are reduced in different ways on a DME: the cationic form is reduced with the consumption of six electrons (at −0.7 to −0.8 V), while the mesoionic form is reduced with the consumption of four electrons (at −1.2 to −1.4 V):



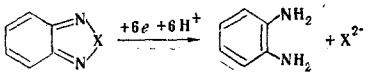
3-Arylsydnonimines [143-145] and N,N'-polymethylenebissydnones [142] are similarly reduced.

Comprehensive investigations of the linear correlation of the $E_{1/2}$ values with the $\sigma$ substituent constants [142, 145] have been made in this series of compounds to prove the aromatic character of the mesoionic sydnone ring; however, these investigations have not led to unambiguous results.

Benzoxazines. 4-Aryl-2,3-benzoxazin-1-ones are reduced in two 2e steps [109, 146]:

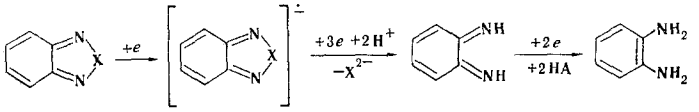


Benzo-2,1,3-X-diazoles. These compounds, particularly benzofurazan, piazothiol, and piazoselenol, are reduced irreversibly in aqueous media with the consumption of six electrons (at −1.2 V), as a result of which the heterocycle is cleaved to give o-phenylenediamine and the corresponding anion ($X^{2-}$) [147-149].



X = O, S, Se

A peculiarity of piazoselenol is the ability of the hydrogen selenide that is formed in acidic media to react with mercury to give an anode wave. In aprotic media [150], all of these compounds also are reduced with the overall consumption of six electrons, but the 1e addition step leading to the formation of quite stable anion radicals can be fixed. The following mechanism for the reduction of benzo-2,1,3-X-diazoles in DMF is proposed:



In this mechanism the first wave (at −1.3 V) corresponds to the first step, the inflection on the second wave corresponds to the second step, and the entire second wave at −2.2 V corresponds to the third step. On the basis of polarographic and adsorption measurements it has been shown that the systems mentioned above have heteroaromatic character; this possibility had been a matter of controversy prior to this [149].

It follows from the data presented above that cleavage of the ring bonds often occurs during polarographic reduction of heteroaromatic systems having several heteroatoms. One should bear in mind that many of the compounds examined are cyclic analogs of hydrazones, azines, oximes, etc., and the principles established during the study of azomethine compounds may therefore also be useful for an understanding of the polarography of heterocycles. However, closing of a cyclic system often substantially changes the course of the reduction both because of the altered reactivity and because of the change in the adsorbability of the cyclic compound as compared with the noncyclic compound.

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