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Electroreduction of Some Diazine and Triazine Pesticides at the Dropping Mercury Electrode

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Electroanalytical methods enable determination of electroactive species in nonhomogeneous systems, as limiting currents are little affected by the presence of solid and colloidal particles. An example of such applications of electrochemical methods are studies of binding of toxic substances, such as pesticides, on slightly soluble polymers, such as lignin. To successfully apply polarographic methods for following free pesticides in a slurry of lignin, it is first necessary in principle to elucidate the electrochemical processes involved. In aqueous buffered solutions the electron transfers, in which organic compounds participate, are in the majority of cases accompanied by chemical reactions. To elucidate the nature of the electrochemical process, it is necessary first to find the pH-region in which the given pesticide is electroactive, i.e., gives a wave on the current-voltage curve, and to determine the number of electrons transferred. Further information is obtained from dependences of limiting currents and half-wave potentials on pH. Such investigations, combined with spectrochemical determination of equilibrium constants and identification of products formed by controlled potential electrolyses, enable recognition of the sequence of chemical and electrochemical steps. In the examples presented, the reduction of the ethylenic bond in maleic hydrazide (I), and reductions of azomethine bonds ($>C=NH^+$ – in some diazine and triazine pesticides, are accompanied by acid-base equilibria, by covalent addition of water to C=N double bonds, and by a ring opening. Such studies are demonstrated by elucidation of the pattern of reduction of some 2-aminopyrimidines (sulfometuron methyl, II), a 1,3,5-triazine(hexazinone, III) and two 1,2,4-triazines (metamitron, IVa and metribuzin, IVb).

Introduction

One of the advantages of polarographic analyses is the possibility of carrying out determinations of electroactive species directly in nonhomogeneous systems. In numerous instances, the limiting currents, as obtained for example by dc or normal pulse polarography, are little affected by the presence of dispersed solid or colloidal particles^{1,2}. An example of such applications of polarography are studies of the binding of various inorganic³ and organic^{4–10} compounds on lignin. Such an approach proved to be particularly useful in

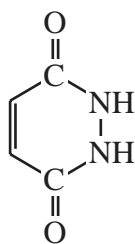
investigations of the binding of various pesticides on natural and commercial lignins, where the use of the dropping mercury electrode enabled direct determination of the free pesticide in highly colored suspensions of lignin⁸⁻¹⁰.

In order to use properly any analytical method, both the physical processes and the chemical reactions involved should be understood. It is insufficient, for example, for a spectrophotometric analytical procedure, to observe formation of an absorbing species under empirically established conditions and to measure absorbance at a chosen wavelength without identifying the structure of the absorbing species and without understanding the nature of reactions by which such species are formed. Only when the chemical composition of the chromophore, the kinetics of its formation and the equilibria involved are understood, is it possible to develop a reliable analytical procedure. For such procedures the matrix effects can be predicted and/or interpreted.

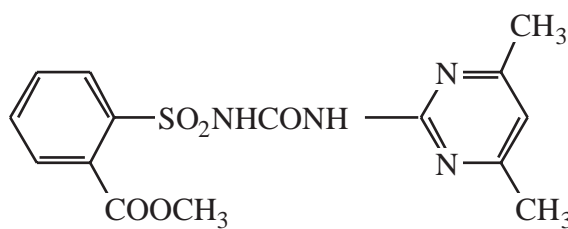
Such principles for development of analytical procedures apply also to those using electroanalytical techniques. In the sequence of electrochemical and chemical steps of an electroanalytical process it is perhaps not necessary to determine the rate of constants of all reactions involved or to determine the values of all equilibrium constants. For analytical applications, nevertheless, the number of consecutive electron transfers, the number of electrons transferred in each of them and the nature of the accompanying chemical reactions should be understood. In aqueous solutions, often encountered in practical analysis, particularly the role of proton transfers, occurring either before or after electron transfers, should be understood.

Hence, before attempting to use dc or differential pulse polarographic curves for determination of pesticides in suspensions of lignin, it was necessary to elucidate the pattern of electrochemical and chemical processes involved in their reduction. As some of the investigated compounds belonged to classes of compounds which have previously been studied only cursorily or not at all, our investigations may also contribute to a better understanding of courses of organic electrode processes and can form a background for detailed studies using more sophisticated electrochemical techniques.

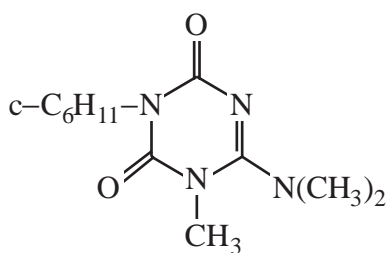
Examples of applications of polarography to the investigation of electroreduction of some pesticides in aqueous buffered solutions are reductions of maleic hydrazide¹¹ (I), sulfometuron methyl¹² (II) and of 3 triazine derivatives: hexazinone¹³ (III), metamitron¹⁴ (IVa), and metribuzin¹⁵ (IVb). As often encountered in the reduction of organic compounds in aqueous media or mixtures of water with organic solvents, the electron transfers are complicated by (a) adsorption of the oxidized or reduced form or of both and (b) chemical reactions such as acid-base, or hydration-dehydration equilibria, or ring opening.



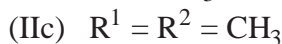
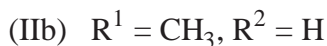
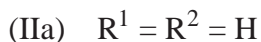
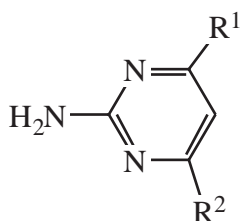
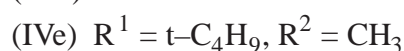
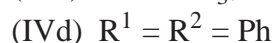
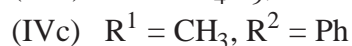
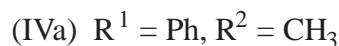
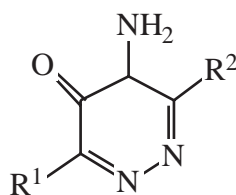
(I)



(II)



(III)



In electrochemical investigations where the goal is to understand the chemical changes of investigated compounds, adsorption often presents an unwanted complication. Attempts are often made to minimize its role, particularly by decreasing the concentration of the electroactive species and/or by using an organic co-solvent. By using these 2 approaches, the effects of adsorption on measurements with the dropping mercury electrode were minimized in all studies that are discussed below. It may be pointed out that measurements with the dropping electrode are in general less affected by adsorption phenomena than measurements carried out with a constant surface electrode, as used in linear sweep or cyclic voltammetry.

As a general rule in electrochemistry, an acid form is always reduced at more positive potentials (i.e., easier) than its conjugate base. If the conjugate acid is reduced at a pH where the base predominates in the solution, additional acid can be formed by protonation of the base close to or at the electrode surface. In investigated compounds the transfer of the first electron is preceded either by a surface protonation of the C=C bond in I, or that of C=N bonds in II-IV.

If a C=O or C=N bond adds covalently water, the resulting adduct is usually not electroactive. For compounds II-IV it has been shown here, that C=N bonds add water or alcohols similarly as in the better-known addition reactions of carbonyl groups. The hydrated forms ($>\text{C}(\text{OH})-\text{NH}-$) of studied compounds are not reducible. The limiting currents of reductions of studied azomethine groups depend both on the position of the hydration-dehydration equilibrium and on the rate of the dehydration reaction. If the position of the hydration-dehydration equilibrium can be established either spectrophotometrically or using cyclic voltammetry at sufficiently high scan rates, the rate of the hydration can be calculated.

As the acid form is always reduced at more positive potentials than the conjugate base, an antecedent acid-base equilibrium is manifested by an increase of a wave *at more positive* potentials with decreasing pH. If, on the other hand, with increasing acidity of the solution, an increase of a wave *at more negative*

potentials occurs, an involvement of a simple acid base equilibrium can be ruled out. Such behavior can be interpreted as due to an acid-catalyzed formation of a species, which is less readily reduced than the parent species. For some of the studied triazine derivatives, reductions of acyclic forms may be less activated than those of heterocyclic species. Thus the decrease of the wave of the reduction of the heterocyclic with increasing acidity and formation of a new wave at more negative potentials seems to be plausibly interpreted as due to a ring opening, resulting in a less conjugated, less easily reduced acyclic form.

Experimental

The properties and provenience of the chemicals, used, both as electroactive species and as supporting electrolytes have been described elsewhere¹¹⁻¹⁵.

D.c. polarographic current-voltage curves were recorded using a 2-electrode configuration; those obtained by differential pulse polarography a 3-electrode configuration. As the reference electrode a saturated calomel was used and as the counter electrode a platinum foil was employed. Properties of the indicator electrodes used have been described elsewhere¹¹⁻¹⁵.

For simple dc polarography the oxygen was removed from 10 ml of buffer or a solution of strong acid or strong base usually containing 30% acetonitrile by purging using a stream of nitrogen or argon. After deoxygenation typically 0.1 ml of a freshly prepared 0.01 M stock solution of the pesticide in acetonitrile was added. After brief (15-30 s) purging by inert gas, current-voltage curves were recorded at a scan rate of 5 mVs⁻¹. All potentials were measured against that of Tl⁺ (-0.46 V) as the internal standard.

Cyclic voltammetric curves were recorded using either a hanging mercury drop electrode (HMDE) or a static mercury drop electrode (SMDE) (Laboratorni Přístroje, Prague) as the working electrode. Scan rates varied between 5 and 200 mVs⁻¹.

Controlled-potential preparative electrolyses were carried out in 3-compartment cells on a stirred mercury pool electrode with a platinum foil auxiliary electrode placed concentrically. Cathodic and reference cell compartments were separated by a double-sintered glass junction and the working potential controlled by a potentiostat.

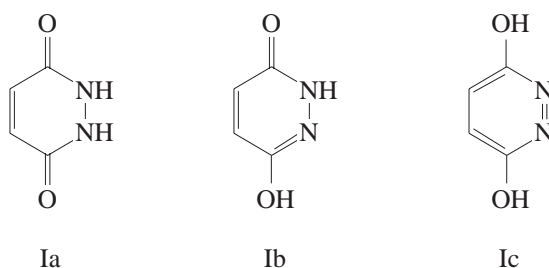
UV-visible spectra of 1×10^{-4} M solutions in aqueous and acetonitrile solutions were recorded in 10 mm cells.

Results and Discussion

Reduction of Maleic Hydrazide (I)

To interpret the changes of polarographic waves of I, it was necessary to consider possible tautomeric equilibria and to interpret the appearance of 4 polarographic waves and the changes of limiting currents and half-wave potentials with pH.

Maleic hydrazide can in principle exist in aqueous solutions in 3 tautomeric forms (Ia-Ic):



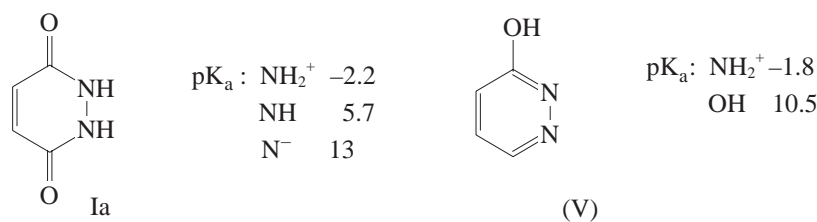
The polarographic reduction of I over the pH range from 0 to 13 occurs in several waves discussed below, but over the entire pH range studied, the total limiting, diffusion-controlled current always corresponds to a single transfer of 2 electrons. Cyclic voltammetry indicated that the 2-electron process is irreversible.

For the tautomeric form Ib it is possible to assume that the reduction first results in a hydrogenation of the C=C double bond, which would be followed by a reduction of the azomethine bond. Thus for the form Ib a total transfer of 4 electrons would be expected, contrary to the 2-electron process observed. Furthermore, the phenolic group in the structure Ib would be prone to an easy oxidation, but no oxidation at potentials more positive than +0.4 V on mercury and than +1.0 V on carbon electrodes was observed. Hence tautomer Ib cannot be the species reduced in observed waves.

The form Ic resembles a p-hydroquinone and, provided that the ring is aromatic, a 2-electron reversible oxidation would be expected. Alternatively, species Ic might be reduced in a 4- or 6-electron process. Both these assumptions are contrary to the observed facts.

Hence, it can be concluded that over the entire pH range various protonated forms of the tautomer Ia are reduced to a dihydro product. Since electrolysis is a dynamic process, which may or may not reflect the position of equilibria existing in the bulk of the solution, it can be concluded that either the form Ia predominates in aqueous solutions or that over the entire pH range the conversion of forms Ib and/or Ic into the reducible Ia is very fast. As rates of establishment of tautomeric equilibria are usually acid-base catalyzed, the second alternative seems less plausible.

The predominance of the tautomer Ia under equilibrium conditions in aqueous solutions is further supported by values of pK_a , corresponding to individual acid-base reactions, as obtained by spectrophotometric or potentiometric measurements. Such a conclusion is based on a comparison of pK_a values of I with those of 3-hydroxypyridazine¹⁶ (V):



Most informative is the process with $pK_a = 5.7$. This acid base equilibrium observed for Ia can be attributed to a dissociation of the ring >NH group, yielding an anion with >N⁻ grouping. No dissociation within the comparable range of pK_a -values has been observed for V.

The process with $pK_a = 10.5$ observed for 3-hydroxypyridazine (V) occurs in a pK_a -range in which most phenolic compounds undergo dissociation. No dissociation of maleic hydrazide (Ia) has been observed in the comparable pH range.

The highest pK_a about 13 observed for compound Ia is absent in solutions of 3-hydroxypyridazine (V). This acid-base equilibrium involving Ia is attributed to the dissociation of the second NH group yielding a dianion.

The pK_a -values found for compounds Ia and V are experimental values obtained by spectrophotometry or titrations, rather than microconstants. It cannot be excluded that measured values involve tautomeric equilibrium constants in addition to microconstants, corresponding strictly to a separation of the proton from a given grouping. But the differences between the pK_a -values larger than 4.0 for Ia and V are sufficiently large to make the contributions of tautomeric equilibria insignificant.

The role of acid-base equilibria in the reduction process is manifested by the changes in limiting currents and half-wave potentials with pH. As mentioned above, in all systems where the electroactive species can exist in a simple acid-base equilibrium, the conjugate acid is always reduced at more positive potentials than its conjugate base. Before discussing the more complex case of the reduction of maleic hydrazide (Ia), where several acid-base equilibria are involved, the role of the simple acid-base equilibria preceding the electron transfer will be discussed first.

For a reducible acid HA which undergoes dissociation (1)



the situation at $\text{pH} < pK_a$, where the acid form HA predominates in the solution, will be discussed first. In this pH range, where the same species which predominates in the solution is reduced, both the wave-height of the wave of HA and its half-wave potential remain pH-independent.

At $\text{pH} > pK_a$, in the pH range where the establishment of equilibrium (1) is fast when compared with the rate of electroreduction, all basic form A^- present in the solution is converted in the vicinity of the electrode into the more easily reducible form HA. Hence the limiting current remains pH-independent, but the half-wave potential is shifted to more negative values with increasing pH [Fig. 1, $\text{pH} < (pK')$].

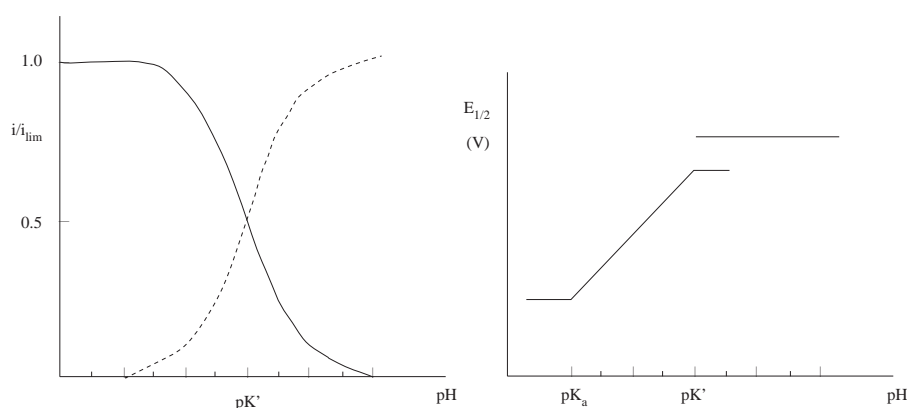


Figure 1. Dependence of polarographic reduction of an acid (HA) and conjugate base (A^-) on pH. (A) Change of the limiting current of the acid (HA) and the base (A^- , dotted line) with pH in systems where equilibrium (1) is rapidly established. (B) Variations of half-wave potentials for the waves of the acid (HA) and base for the same system. pK_a corresponds to the equilibrium constant of the acid-base reaction, pK' equals to pH, where $i = i_d/2$.

Finally, at sufficiently high pH values [at $\text{pH} > (\text{pK}'-2)$] the rate of protonation becomes so slow that it does not convert all of the A^- into HA. This results in a decrease of the limiting current i_{HA} , which is the greater the higher the pH. In this pH range the plot of i_{HA} (or i_{HA}/i_d) as a function of pH has the shape of a decreasing dissociation curve, where $i_{\text{HA}} = i_d/2$ is denoted pK' . At $\text{pH} > \text{pK}'$ the half-wave potential of the acid form HA becomes pH independent (Fig. 1b)

For compounds where the reduction of the conjugate base occurs within the accessible potential range, the wave of the conjugate base A^- increases with increasing pH in the shape of a dissociation curve with an inflexion point at $\text{pH} = \text{pK}'$. If the acid and its conjugate base are reduced by the same number of electrons, the sum of the heights of the acid (HA) and its conjugate base (A^-) remains constant (Fig. 1A). At $\text{pH} > \text{pK}'$ the half-wave potentials of the reduction of the conjugate base (A^-) are more negative than those of the acid HA and usually are pH-independent (Fig. 1B).

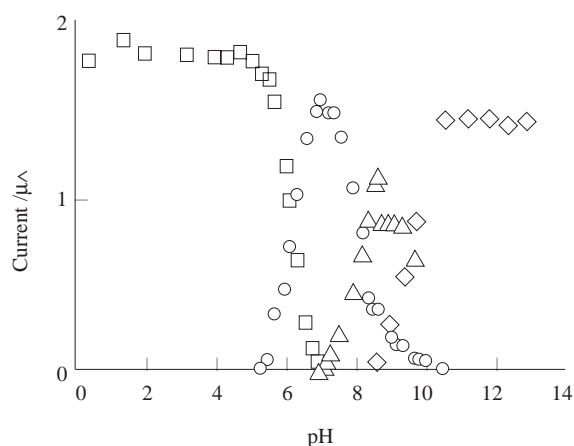


Figure 2. Dependence of dc polarographic limiting currents on pH in buffered solutions of 2×10^{-4} M maleic hydrazide: \square , wave I_1 ; \circ , wave I_2 ; \triangle , wave I_3 ; \diamond , wave I_4 . Reprinted from *Journal of Electroanalytical Chemistry* **420**, 79-87 (1997).

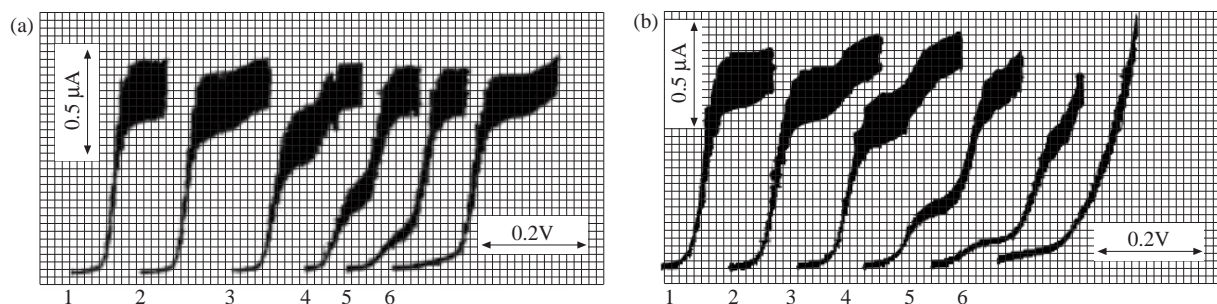


Figure 3. Changes of polarographic waves in buffered solutions of 2×10^{-4} M maleic hydrazide with pH: (a) 1, pH 4.2; 2, pH 5.4; 3, pH 5.9; 4, pH 6.2; 5, pH 6.5; 6, pH 6.9; (b) 1, pH 7.1; 2, pH 7.5; 3, pH 7.8; 4, pH 8.5; 5, pH 9.3; 6, pH 9.9. Curves (a) 1 and 2 starting at -0.9 V, 3 starting at -0.95 V, 4 to 6 starting at -1.0 V; (b) 1 to 3 starting at -1.2 V, 4 starting at -1.25 V, 5 starting at -1.3 V, 6 starting at -1.4 V. Reprinted from *Journal of Electroanalytical Chemistry* **420**, 79-87 (1997).

As maleic hydrazide (Ia) can undergo not one, but 4 acid-base equilibria, the observed dependences of currents, I_1 , I_2 , I_3 and I_4 are more complex (Figs. 2-4): Wave I_1 shows with increasing pH a decrease in the shape of the dissociation curve (Figs. 2 and 3), waves, I_2 and I_3 an increase, followed by a decrease, wave

I₄ a increase. Dependences of half-wave potentials of pH for waves I₁, I₂, and I₃ all show 3 linear segments, that for I₄ are pH-independent (Fig. 4).

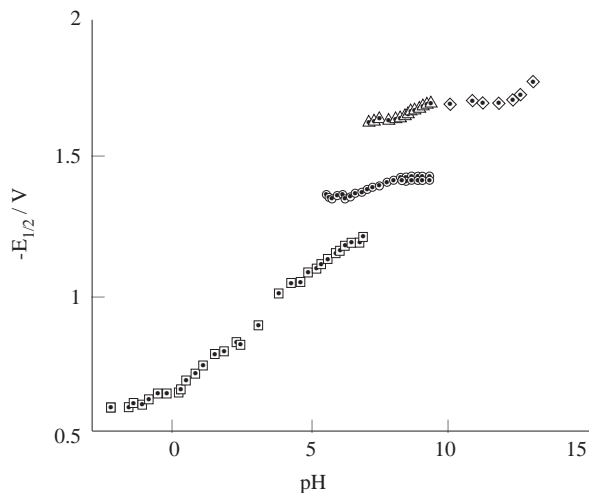
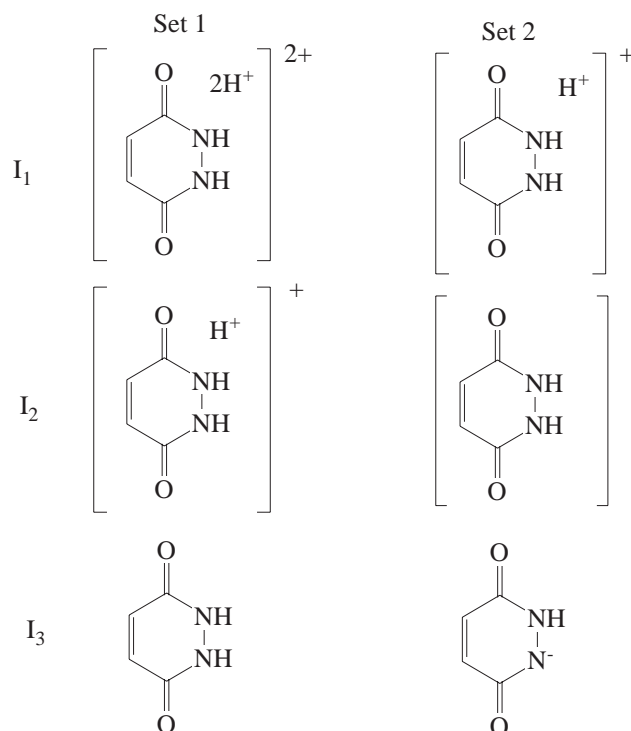
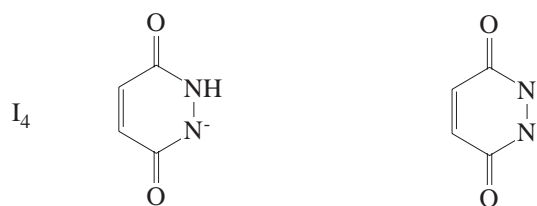


Figure 4. Dependence of half-wave potentials (SCE) on pH in buffered solutions of 2×10^{-4} M maleic hydrazide for \square , wave I₁; \circ , wave I₂; Δ wave I₃; \diamond , wave I₄. Reprinted from *Journal of Electroanalytical Chemistry* 420, 79-87 (1997).

There are two possible sets of attribution of structures to species reduced in waves I₁-I₄:





Structures corresponding to Set 1 are preferred for the following reasons:

(a) The shape of $i = f(\text{pH})$ plot for I_1 is steep. This corresponds to a reduction of a dibasic acid, as $I_1 = f(\text{pH})$ fits well equation (2) derived for dibasic acids^{17,18} (2):

$$I_d/I_d = \frac{0.87(t_1k_1/K_1)^{1/2}\{[H^+]^2/([H^+] + K_2)\}}{1 + 0.87(t_1k_1/K_1)^{1/2}\{[H^+]^2/([H^+] + K_2)\}} \quad (2)$$

rather than equation (3) derived for monobasic acids:

$$I/I_d = \frac{0.87(t_1k/K)^{1/2}[H^+]}{1 + 0.87(t_1k/K)^{1/2}[H^+]} \quad (3)$$

A further condition for the application of eq. (2), namely that pK'_1 (i.e., pH where $I_1 = I_d/2$) is larger than pK_2 , is fulfilled, as $\text{pK}'_1 = 6$ and $\text{pK}_2 = 5.7$.

(b) In Set 2 it is assumed that a dianion is reduced in wave I_4 . Such an assumption is not plausible, because such highly charged negative species would not be reduced at potentials more positive than -2.0 V.

(c) Limiting currents I_2 and I_3 depend not only on pH, but also on the nature of the buffer used and its concentration. Such an increase of the reduction of a conjugate acid with increasing buffer concentration (Fig. 5) indicates that protonation of the conjugate base occurs not only by hydrogen ions, but also by acid buffer components. Such effects have been observed for protonations of other derivatives of α, β -unsaturated carboxylic acids.

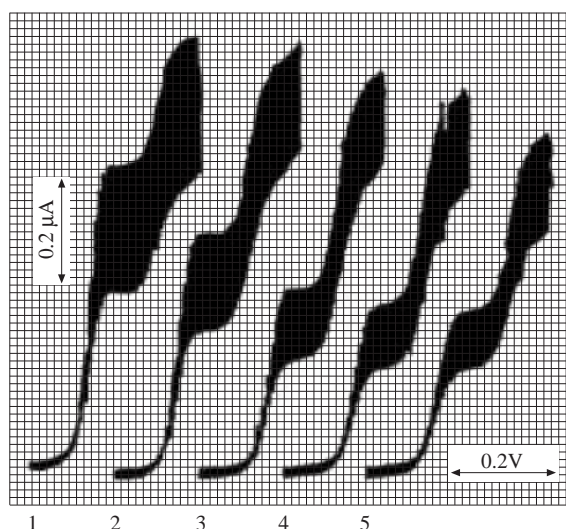


Figure 5. Dependence of limiting currents on buffer concentrations. 2×10^{-4} M maleic hydrazide. Ammonia, ammonium chloride buffer pH 8.4, concentration of buffer 1, 0.1 M/1 M; 2, 0.03 M/0.3 M; 3, 0.1 M/0.1 M; 4, 0.003 M/0.03 M; 5, 0.001 M/0.01 M. Reprinted from *Journal of Electroanalytical Chemistry* **420**, 79-87 (1997).

Whereas the changes in limiting currents and half-wave potentials indicate that protonation takes place before the transfer of the first electron, they do not indicate the site of protonation. This can be concluded from the structure of the product. As in the reduction of Ia, the ethylenic bond is hydrogenated, so it is possible to assume that in the surface protonation it is the ethylenic carbon rather than the amidic nitrogen which is preferentially protonated, similarly as in the reduction of maleic or fumaric acid.

Reduction of Sulfometuron Methyl

To interpret the processes involved in the reduction of sulfometuron methyl (II), its behavior was compared with that of substituted 2-aminopyrimidines (IIa-IIc). For all these 4 compounds a single reduction wave was observed, which can be attributed to the reduction of the protonated form of the azomethine bond ($>C = NH^+ -$). As for systems in which the reduction is preceded by a simple acid-base equilibrium (1), the heights of the waves of all 4 compounds (II-IIc) decrease with increasing pH and the $i = f(\text{pH})$ have the shape of a dissociation curve (Fig. 6). The plots of $E_{1/2} = f(\text{pH})$ (Fig. 7) are somewhat more complicated than those in Fig. 1b discussed above. For all $E_{1/2} = f(\text{pH})$ plots the changes in the slopes of the linear segments are of importance. For irreversible processes the change from a smaller to a large slope corresponds to an acid-base equilibrium in the bulk of the solution. The pH at the intersection between a linear segment with a smaller slope and a linear segment with a large slope corresponds to a pK_a -value. But a change from a larger to a smaller slope occurs in a pH range where the rate of protonation is not sufficiently fast. The intersection of a segment with a larger slope with a segment with a smaller slope occurs at $\text{pH} = \text{pK}'$, also obtained from $i = f(\text{pH})$ plots at pH where $I = I_d/2$. In the particular case of the 2-aminopyrimidine derivatives studied, the $E_{1/2} = f(\text{pH})$ plot shows 4 linear segments with slopes 0.0 V/pH; 0.06 V/pH; 0.12 V/pH and 0.0 V/pH (Fig. 7). The pH values at the first 2 intersections correspond to pK_1 and pK_2 of the compound studied. The third intersection, at a pH where the slope decreases from 0.12 V/pH to 0.0 V/pH, corresponds to pK' (i.e., pH at which $I = I_d/2$).

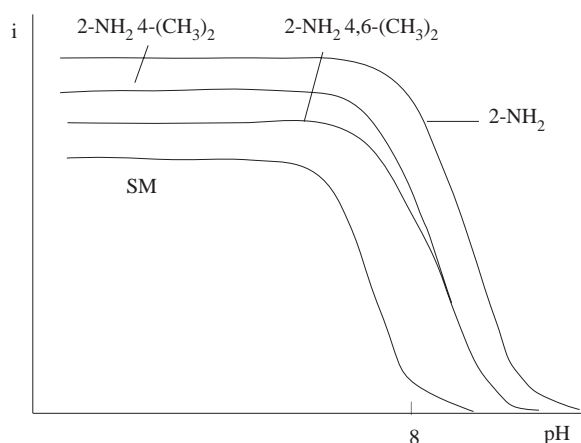


Figure 6. Dependence of limiting currents of some 2-aminopyrimidines on pH. Buffered solutions of 2×10^{-4} M piperidine derivatives (1) II; (2) IIa; (3) IIb; (4) IIc. Substituents indicated. SM - sulfometuron methyl.

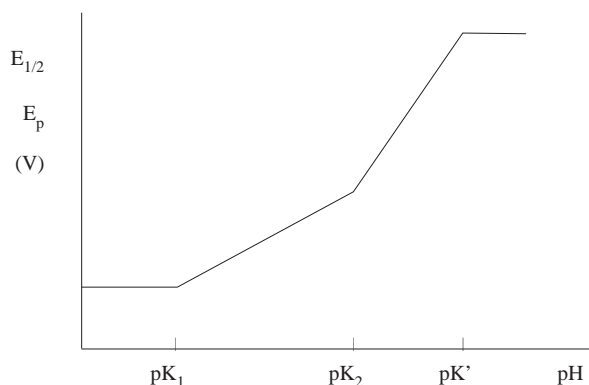


Figure 7. Schematical dependence of half-wave potentials of sulfometuron methyl (II) on pH. pK_1 and pK_2 correspond to two dissociation constants of II, pK' to pH, where $i = i_d/2$

Second, a more important difference between the behavior of compounds II-IIc and that of simple reducible acid formed according to eq. (1), involves currents in the pH range [at $\text{pH} > (\text{pK}' - 2)$] where the pre-protonation is fast and the current remains pH-independent over several pH units. In this pH range currents of all compounds II-IIc are significantly smaller than would correspond to a 2-electron diffusion controlled process. Moreover, the size of the decrease depends on the nature of substituents on the pyrimidine ring (Fig. 6). After excluding the possibility that such reproducible decreases might be due to impurities in available specimens and proving that the observed decreases differ much more than can be attributed to variations in diffusion coefficients, the possibility of interaction of electroactive species with solvent was considered.

Covalent addition of water and alcohols to C=O double bonds is well known, but analogous nucleophilic additions to azomethine bonds has received much less attention²⁰⁻²², and was more extensively studied only for some pteridines²³ and quinazoline²⁴. Few values of equilibrium constants for such reactions are available. As such covalent additions to azomethine bonds, postulated here for 2-aminopyrimidines, were observed (as discussed below) to occur also in solutions of some 1,2,4- and 1,3,5-triazines, it seems that the phenomenon occurs more widely than anticipated.

To prove that the decrease of the limiting current at $\text{pH} < (\text{pK}' - 2)$ is due to addition of water, solutions were prepared containing a constant concentration of the 2-aminopyrimidine derivatives and varying concentrations of acetonitrile. An increase from 0% to 60% v/v of acetonitrile at pH 3.7 resulted in an increase in the limiting current of sulfometuron methyl (II) by 40% (Fig. 8). This increase was observed in a pH range where a change in the activity of hydrogen ions within ± 1.0 pH units does not affect the limiting current. It is known that the pH value of buffers at pH 3.7 does not change by more than 0.3 pH units when the concentration of acetonitrile is changed from 0% to 50% v/v. This indicates that in aqueous solution at least 40% of compound II is present in hydrated form.

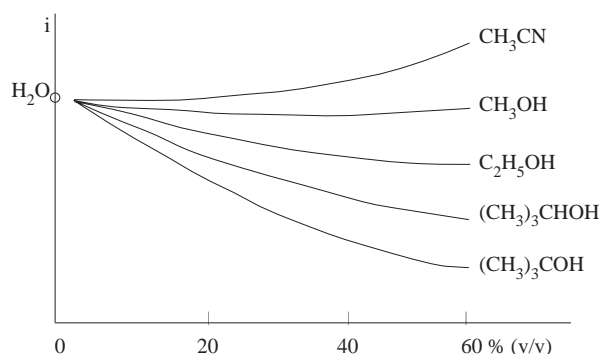
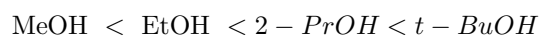


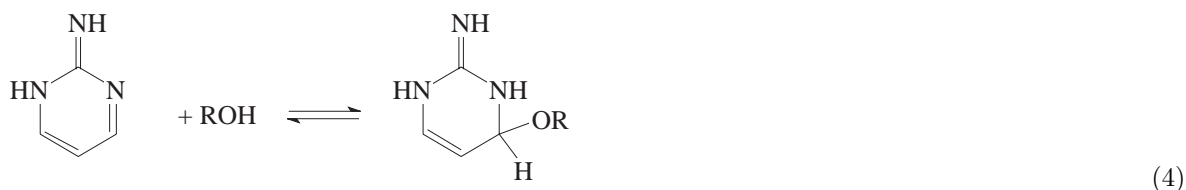
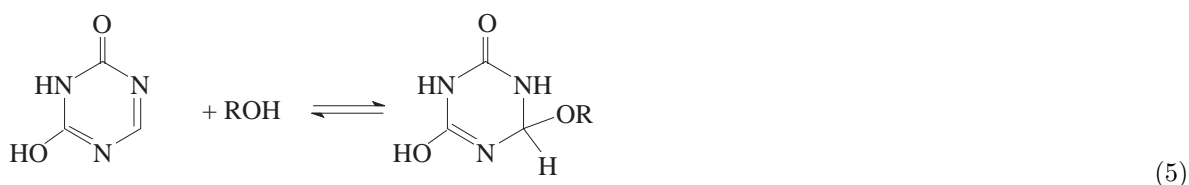
Figure 8. Dependence of the limiting current of 2×10^{-4} M sulfometuron methyl (II) on concentration of organic co-solvent (in % (v/v)). Solvent : (a) CH_3CN ; (b) CH_3OH ; (c) $\text{C}_2\text{H}_5\text{OH}$; (d) $2\text{-C}_3\text{H}_7\text{OH}$; (e) $t\text{-C}_4\text{H}_9\text{OH}$.

A change in the limiting current in the opposite direction occurs when water is gradually replaced as solvent by alcohols. As the equilibrium in the presence of alcohols is shifted in favor of the adduct more than in water, a decrease in current of II (corrected for changes in viscosity) is observed with increasing concentration of the alcohol (Fig. 8). The stability of the adduct increases in the sequence:



Addition of water and alcohols to II has also been confirmed spectrophotometrically. Such additions

(4)

resemble additions of ROH to 5-azauracils²⁵ (5):

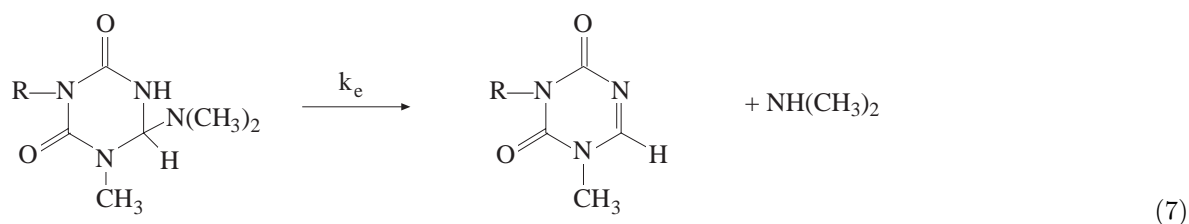
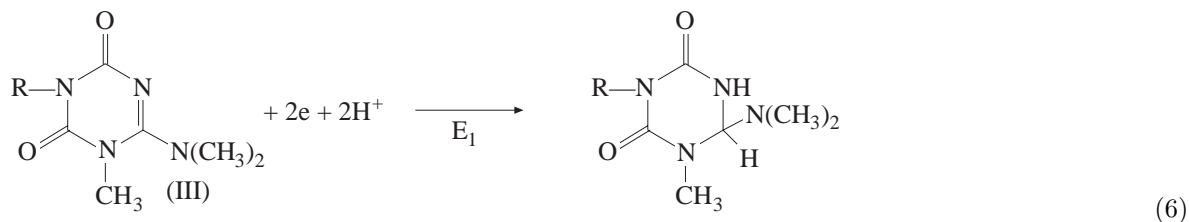
where the binding of ROH is so strong that it was possible to isolate the adducts.

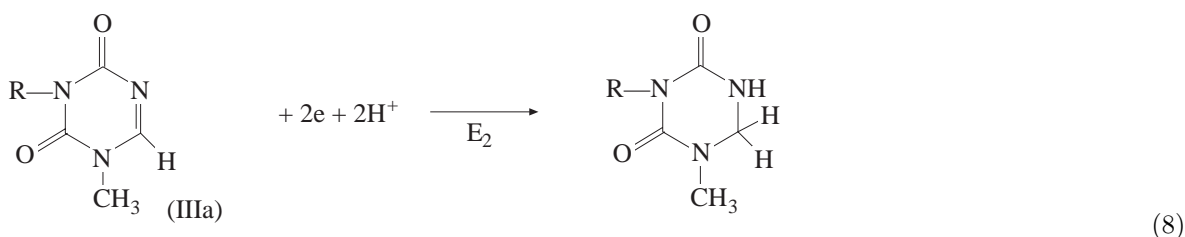
From pH values of the intersection of linear segments of $E_{1/2} = f(\text{pH})$ plots it is possible to estimate values of pK_2 . These values are in good agreement with data obtained spectrophotometrically:

$\text{pK}_2/\text{Compound}$	II	IIa	IIb	IIc
Polarography	5.2	3.5	4.2	4.2
Spectrophotometry	5.0	3.5	4.5	5.0

Reduction of 1,3,5-Triazines

Reduction of hexazinone (III) is representative of such 1,3,5-triazines which can exist only in one tautomeric form, indicated by structure III. The electrochemical behavior of this compound manifests one peculiarity: even when the compound bears only a single azomethine group and no other easily reducible grouping, it is reduced in two 2-electron waves. Moreover, above pH 1.5 both the currents and half-wave potentials of both of these waves show changes with pH that are so similar, that the electrochemical processes in both these steps must involve conversion of the same electroactive group. This can be interpreted by the following set of reactions (6)-(8) summarizing the overall processes (R = cyclohexyl):





The elimination reaction (7) with the rate constant k_e is sufficiently fast to convert all of the dihydro compound into the azomethine species during the life of a single mercury drop (about 3 s). It has been pointed out to us by Lund²⁶ that in some other systems he studied, such eliminations can be sufficiently fast. As in reactions (6) and (8) the same azomethine bond is reduced, only in a slightly different environment, it is possible to understand the similarity of shapes of both $i = f(\text{pH})$ (Fig. 9) and $E_{1/2} = f(\text{pH})$ (Fig. 10) plots. The substituent effect of $\text{N}(\text{CH}_3)_2$ in the reduction (6) compared to (8) results in a shift of 0.1 V to 0.15 V to more positive potentials.

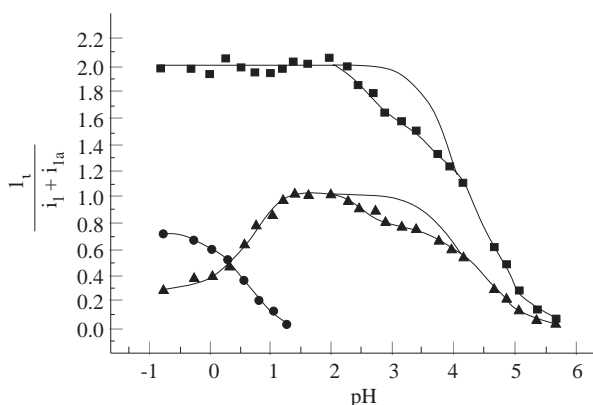


Figure 9. Variation of limiting currents for the reduction of hexazinone with pH. Squares, $I_l = (I_1 + I_{1a} + I_2)$; triangles, $I_l = I_1$; circles $I_l = I_{1a}$. Lines correspond to currents in the absence of hydration. All solutions contain $1 \times 10^{-4} \text{ M}$ hexazinone and 1% v/v acetonitrile. Dc polarographic working electrode-DME with a Smoler capillary ($m = 0.64 \text{ mg s}^{-1}$ and $t_1 = 1.9 \text{ s}$ at $h = 72 \text{ cm}$ in 0.1 M KCl at 0.0 V vs SCE). Scan rate $\nu = 5 \text{ mV s}^{-1}$. Reprinted from *Journal of Electroanalytical Chemistry* **455**, 235-246 (1989).

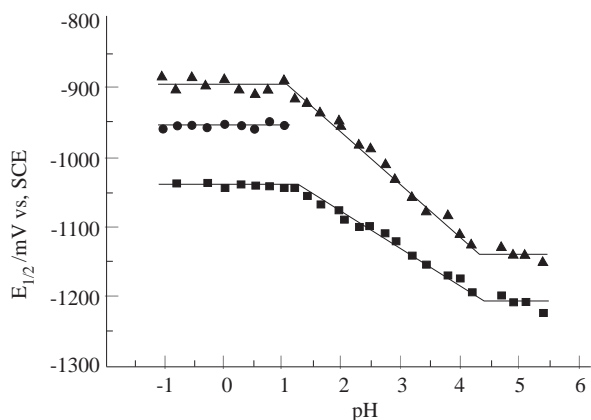
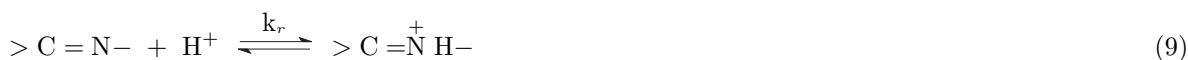


Figure 10. Variation of polarographic half-wave potentials $E_{1/2}$ with pH. Triangles $(E_{1/2})_1$; circles $(E_{1/2})_{1a}$; squares $(E_{1/2})_2$. All solutions contain $1 \times 10^{-4} \text{ M}$ hexazinone and 1% v/v acetonitrile. Working electrode-DME with a Smoler capillary ($m = 0.64 \text{ mg s}^{-1}$ and $t_1 = 1.8 \text{ s}$ at $h = 72 \text{ cm}$ in 0.1 M KCl at 0.0 V vs SCE). Scan rate $\nu = 5 \text{ mV s}^{-1}$. Reprinted from *Journal of Electroanalytical Chemistry* **455**, 235-246 (1998).

As in other examples of reductions of azomethine bonds in the literature²⁷⁻²⁹ and in this contribution, the reduction involves the protonated form:

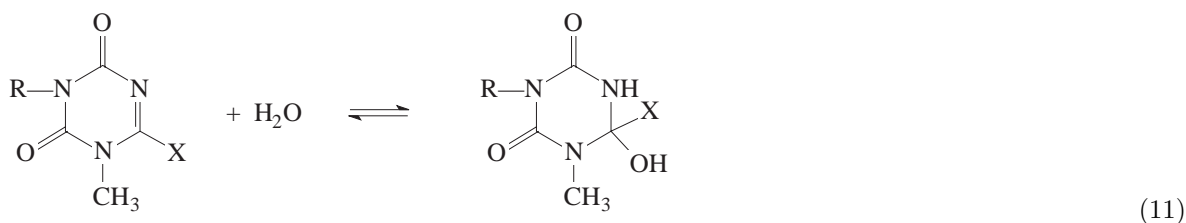


As long as the rate of protonation (9) with the constant k_r is sufficiently fast to convert all the azomethine bonds in the vicinity of the electrode into corresponding acids, the limiting current (corresponding

to a 2-electron diffusion controlled process) remains pH-independent. With pH increasing above 3, the decrease in the rate of protonation results in a decrease of the limiting current. The plot of $i = f(\text{pH})$ has the shape of a decreasing dissociation curve (Fig. 9). In the same pH range, the half-wave potential becomes pH-independent (Fig. 10).

In strongly acidic media with increasing acidity the half-wave potentials become pH-independent at $\text{pH} < 1.2$, which corresponds to pK_a 1.2 obtained for reaction (9) by spectrophotometry.

For both waves the current at pH 2 to 4 is lower than the theoretical value corresponding to a 2-electron diffusion controlled process (6) or (8) preceded by a rapidly established equilibrium (9). This decrease is attributed to a covalent addition of water to the 2,3-azomethine bond, both in the parent compound III and its analog, IIIa, formed by elimination from the dihydroderivative. In both cases the current at pH 3.5 corresponds to 81% of the diffusion current. As the current at this pH does not depend only on the concentration of the unhydrated form in equilibrium, but also on the rate by which this form can be generated by dehydration in the vicinity of the electrode, it is possible to estimate the upper limit of the equilibrium constant of reaction (11):



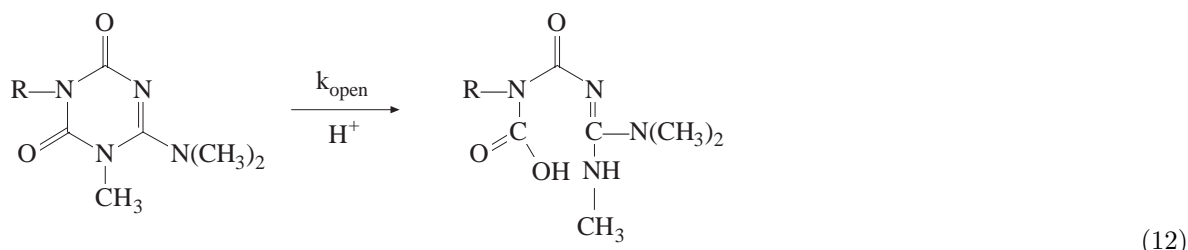
(where $\text{X} = \text{N}(\text{CH}_3)_2$ for III and $\text{X} = \text{H}$ for IIIa)

For both compounds $K_d = [\text{C}=\text{N}]/[\text{C}(\text{OH})-\text{NH}]$ is smaller than 4.3. More accurate determination of the value of K_d using linear sweep voltammetry is prevented by a strong adsorption of II on a mercury electrode with unrenewed surface, such as the hanging mercury drop electrode.

The increase of current with increasing acidity at pH lower than about 3 is attributed to an increase in the rate of dehydration, which is acid catalyzed. Due to acid catalysis at pH between 2 and 1 for III and between pH 2.5 and $\text{H}_o = -1$ for IIIa the rate of dehydration is sufficiently fast to convert all hydrated into electroactive unhydrated form, yielding a 2-electron diffusion controlled current.

It remains to discuss the decreases in current of III at $\text{pH} < 1$ with increasing acidity (Fig. 9). The decrease observed in the wave I_1 with decreasing pH is accompanied by an increase of another wave *at more negative potentials* than I_1 . As a conjugate acid would be reduced *at more positive potentials*, the decrease at $\text{pH} < 1$ cannot be attributed to a simple acid-base equilibrium. Rather the observed changes with varying acidity can be attributed to formation of a species, which is less easily reduced than the parent compound. Moreover, the reaction which yields this new electroactive species must be acid catalyzed. It is proposed

that such a reaction is an acid-catalyzed ring opening, such as (12):

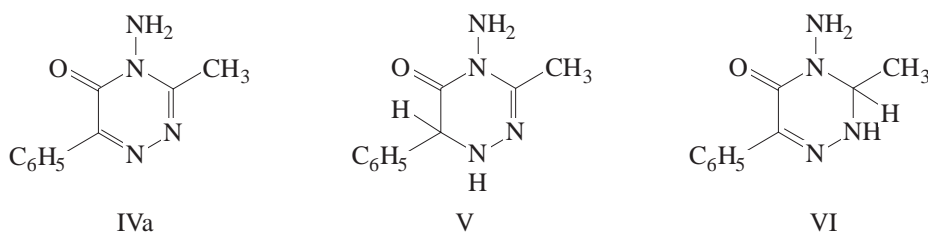


The more negative observed could be attributed either to the reduction of the product of reaction (12) or to that of products of rapid hydrolysis, consecutive to (12).

To minimize the adsorption effects, the experiments were carried out at concentrations of hexazinone (III) lower than 5×10^{-5} M. The use of organic co-solvents, such as alcohols or acetonitrile, was limited to about 20% v/v of the organic component. At a higher content of the organic component of the solvent, the electrode process becomes more complex.

Reduction of Some 1,2,4-Triazines

To interpret the electrochemical behavior of pesticides metamitron (IVa) and metribuzin (IVb) some analog compounds (IVc)-(IVe) were prepared and studied^{14,15}. In buffered aqueous solutions of all these compounds two 2-electron waves were observed, which had similar characteristics. The half-wave potentials, their dependence on pH and the variations of limiting currents with pH for compound IVa were compared which such data obtained for authentic samples of the 1,6-dihydroderivative (V) (prepared electrochemically) and of the 2,3-dihydroderivative (VI) (prepared chemically by reduction with sodium borohydride).



Such comparison led to the conclusion that in the first reduction step for IVa the C=N double bond in position 1,6- is hydrogenated and in the second the C=N double bond in position 2,3-. The reduction of the azomethine bond in position 1,6- occurs over the entire pH range at potentials by more than 0.5 V more positive than that of the azomethine bond in position 2,3- (Fig. 11). This enhancement of reducibility is attributed to the effect of conjugation of the 1,6-azomethine group with the amidic carbonyl group in position 5. This effect is much larger than that of the substituent on C-6, as the difference between the ease of reduction of the C=N bond in 1,6- and 2,3-positions is little affected by replacement of 6-C₆H₅ in IVa for an alkyl group in IVb, IVc or IVe.

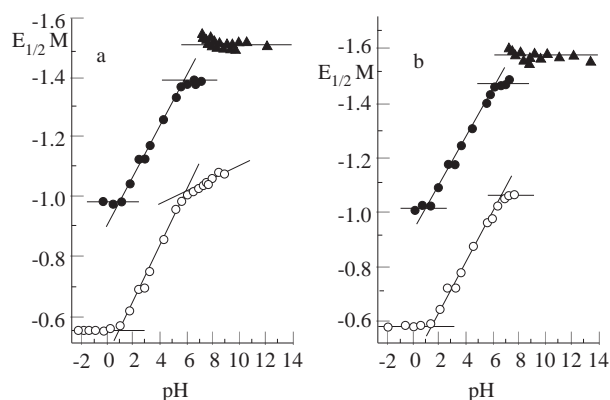
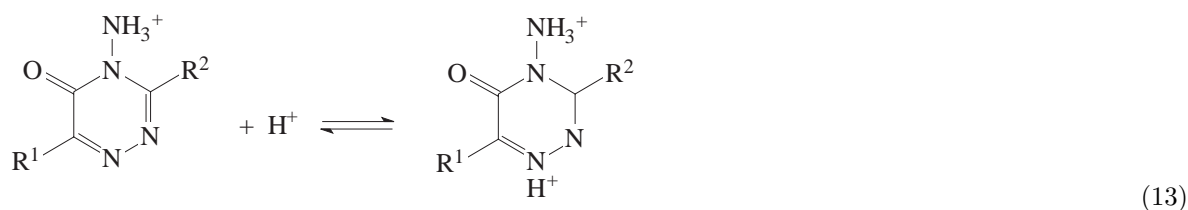


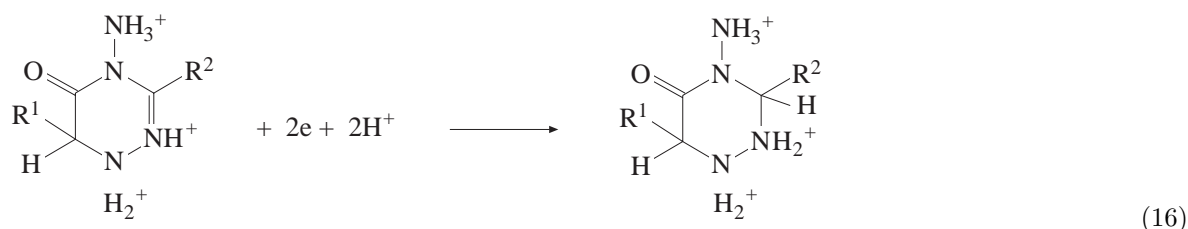
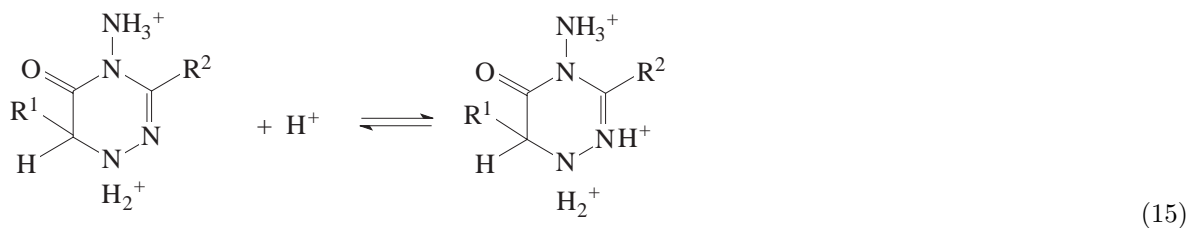
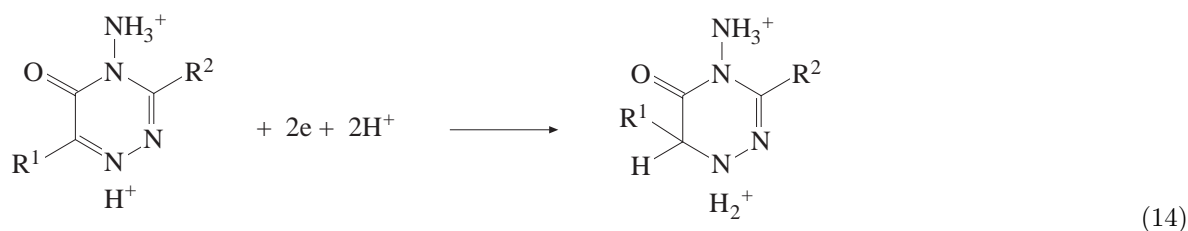
Figure 11. a) Dependence of the DC-polarographic half-wave potentials ($E_{1/2}$) of the first and the second reduction step of metribuzin (I) on pH. (Concentration of the triazine 2×10^{-5} M, 30% v/v acetonitrile-aqueous buffer mixtures). ○) wave i_1 ; ▲) wave i_{1A} ; ●) wave i_2 . b) Dependence of peak potentials obtained by cyclic voltammetry (E_p) of the first and the second reduction step of metribuzin (I) on pH. (Concentration of the triazine 2×10^{-5} M, 30% v/v acetonitrile-aqueous buffer mixtures). ○) peak corresponding to wave i_1 ; ▲) peak corresponding to wave i_{1A} ; ●) peak corresponding to wave i_2 . Reprinted from *Journal of Electroanalytical Chemistry* **457**, 177-190 (1998).

As in the case of hexazinone (III), the reductions of azomethine bonds in all studied 1,2,4-triazines (IVa-IVe) are accompanied by pre-protonation. At pH lower than 4 this protonation occurring in the vicinity of the electrode is able to convert all of the 1,2,4-triazine into the electroactive protonated form and the 2-electron limiting current is diffusion controlled. When the rate of the protonation becomes with increasing pH insufficient to convert all the C=N bonds into protonated forms, the limiting current decreases with increasing pH. The plot of the dependence of this current on pH has the shape of a decreasing dissociation curve (Fig. 12). The pattern is similar for reductions of both the 1,6- and 2,3-azomethine bond. The conjugate base that is not protonated on the 1,6-bond is reducible in the accessible potential range. Thus the decrease of the wave of the protonated form of the 1,6-azomethine bond is accompanied by an increase of a 1-electron wave of the conjugate base (Fig. 12).

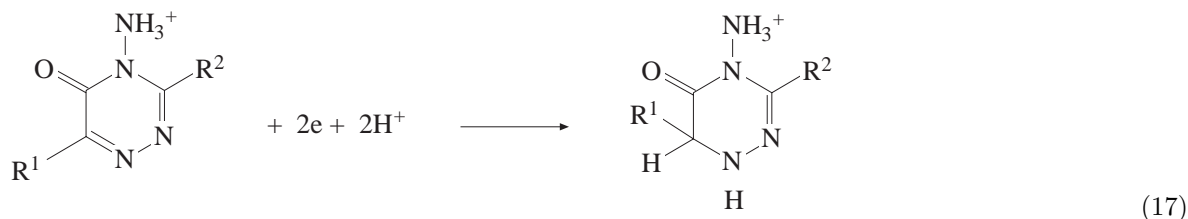
For the 2,3-azomethine bond, where even the reduction of the protonated form occurs at considerably more negative potentials than that of the 1,6-bond, the reduction of the unprotonated 2,3-bond occurs at such negative potentials that it is not accessible for measurement.

The overall scheme of the reduction of 1,2,4-triazines IVa-IVc follows for the protonated forms the pattern (13)-(16):

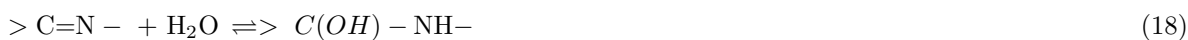




and for the 1,6-bond in the unprotonated form reaction (17):



Between pH 1 and 6 for metamidron (IVa) (Fig. 12a) and between pH 2.5 and 5.5 for 2,3-dihydropyrimidin-4(1H)-one (VI) Fig. 12b) the limiting current is lower than would correspond to a 2-electron diffusion-controlled process. This pattern is similar to that of hexazinone (III) discussed above and is similarly attributed to a covalent addition of water to the 1,6-azomethine bond (18):



The increase of current at pH < 3 for metamidron (IVa) and at pH < 4.5 for the 2,3-dihydroderivative (VI) with decreasing pH corresponds to an increase in the rate of the acid catalyzed dehydration with decreasing pH. The rate of dehydration is faster when it occurs at the electrode surface for IVa than when it occurs in solution in the vicinity of the electrode for VI.

At pH 6 the measured current corresponds to about 80% of the theoretical value for a 2-electron diffusion-controlled process. As these currents may be dependent on the rate of the dehydration, in addition to the position of the equilibrium (18), only the upper limit of the dehydration equilibrium constant, $K_d = [\text{C}=\text{N}]/[\text{C}(\text{OH})\text{NH}]$ can be estimated as $K_d = 4.0$.

No measurable decrease has been observed for the limiting current of the reduction of the 2,3-azomethine bond. Hence either this bond is less strongly hydrated or the rate of dehydration is higher.

The attribution of the decrease of the limiting current at pH 1 to 6 for metamitron (IVa) is further supported by the changes in current in the presence of aliphatic alcohols. The decrease in current of the metamitron (IVa) at pH 4, corrected for changes in viscosity in solutions containing 30% v/v alcohol increases in the sequence



which parallels the sequence of nucleophilicity of these alcohols.

The 1,2,4-triazine ring in the parent compound (IVa) does not undergo hydrolysis and is stable up to $H_o = -1$. For its 1,6-dihydroderivative (V), either formed at the electrode surface (Fig. 13a) or added to the solution (Fig. 13b), is observed a decrease in the 2-electron limiting current at pH lower than 3.5. This decrease is chemically reversible, i.e., when the pH is increased above 4, the 2-electron wave is again observed. This decrease with increasing acidity of the reduction of the protonated 1,6-azomethine bond is accompanied by an increase in a wave *at more negative potentials* (Fig. 13). This can be attributed, as in the case of hexazinone (III), to an acid-acatalyzed ring opening, followed by a reduction either of the straight-chain form or a product of its rapid cleavage. Studies of these compounds using cyclic voltammetry did not yield additional information.

Role of Conjugation in the System $\text{C}=\text{N}-\text{N}=\text{C}$

In organic molecules bearing conjugated double bonds of the types $\text{C}=\text{C}-\text{C}=\text{C}$; $\text{C}=\text{C}-\text{C}=\text{O}$; $\text{C}=\text{C}-\text{C}=\text{S}$; $\text{C}=\text{C}-\text{C}=\text{N}$; $\text{O}=\text{C}-\text{C}=\text{O}$; $\text{O}=\text{C}-\text{C}=\text{N}$; and $\text{N}=\text{C}-\text{C}=\text{N}$ conjugation results in delocalization of π -electrons involved. As a result, the distance between the central $\text{C}-\text{C}$ atoms is significantly shorter than in saturated compounds. In electrochemistry, the delocalization is manifested by a shift of the reduction of the $\text{C}=\text{C}$, $\text{C}=\text{O}$, $\text{C}=\text{N}$ or $\text{C}=\text{S}$ group to more positive potentials, attributed to a resonance effect.

The behavior of 1,2,4-triazine derivatives IVa-IVe shows a remarkable deviation from such effects. The half-wave potentials of metamitron¹⁴ (IVa), which correspond to the reduction of the 1,6-azomethine group, are within ± 2 to 3 mV identical over the entire pH range studied from pH 1 to 10 with half-wave potentials of the reduction of the 1,6-azomethine bond in 2,3-dihydrometamitron (VI), prepared by a chemical reduction (Fig.13). Furthermore, the half-wave potentials of the reduction of the 1,6-azomethine bond are practically unaffected by the nature of the substituent on C-3. They remain unchanged if there is a methyl, phenyl, or a thiomethyl group in position 3.

These observations indicate that the reduction of 1,6- $\text{C}=\text{N}$ group is practically unaffected, if in position 2,3-there is either a $\text{C}=\text{N}$ or a CHNH group and by changes in distribution of electron density on the 2,3- $\text{C}=\text{N}$ bond resulting from substituents on C-3. Thus whereas a central $\text{C}-\text{C}$ bond in a conjugated system is involved in delocalization of electron density, such delocalization is at least very limited over the central $\text{N}-\text{N}$ bond in the ring system including a $\text{C}=\text{N}-\text{N}=\text{C}$ grouping.

The lack of delocalization is further supported by preliminary MO calculations and X-ray crystallography, which indicate absence of overlap of orbitals on N-1 and N-2 and a practically single bond character of the $\text{N}-\text{N}$ bond. Our current investigations were designed to resolve whether such a lack of delocalization is restricted to the type of heterocyclic compounds studied or can be observed even for acyclical compounds.

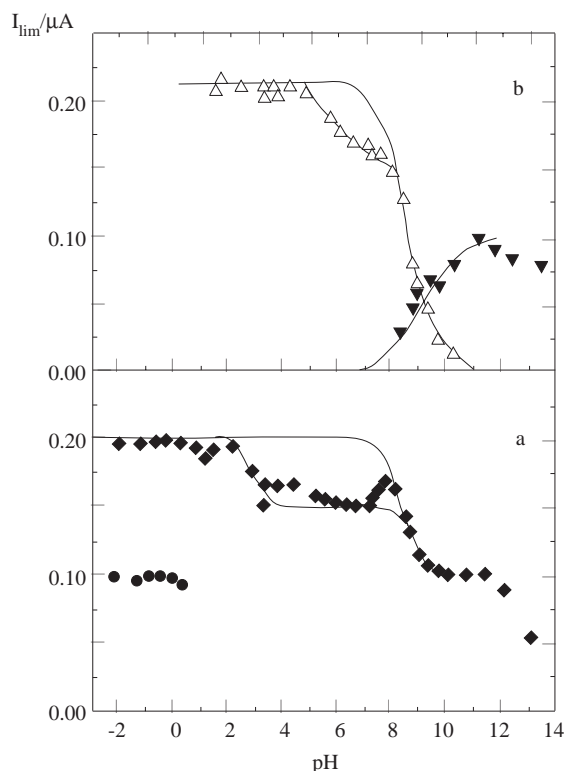


Figure 12. Comparison of the dependence of limiting currents on pH in 3×10^{-5} M solutions of triazines in aqueous buffers containing 0.3% (v/v) acetonitrile. (a) Reduction of metamitron (IV_a): (◆) wave I₁ or at pH < 0.5 the sum of I_{1a} + I_{1b}; (●) wave I_{1b}. (b) Reduction of 2,3-dihydrometamitron (VI): (△) wave I₁ (separation of I_{1a} and I_{1b} at pH < 0.5 observed but current measurement prevented by hydrolysis); (▼) wave I_{1A}. Currents corrected for variations in viscosity. Reprinted from *Journal of Electroanalytical Chemistry* **457**, 177-190 (1998).

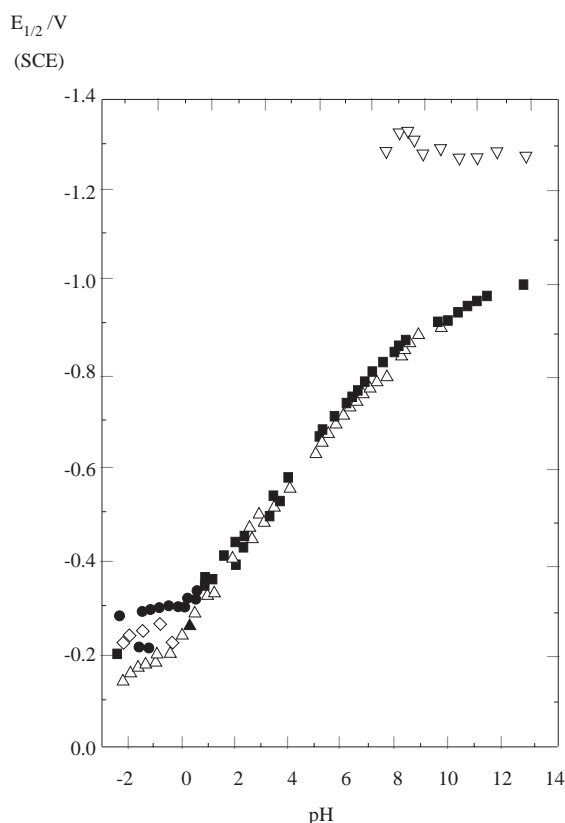


Figure 13. Comparison of the dependence of limiting currents on pH in 3×10^{-5} M solutions of triazines in aqueous buffers containing 0.3% (v/v) acetonitrile. (a) Reduction of metamitron: waves I₁ and I_{1a} (at pH < 0.5): (●) wave I_{1b}. Reduction of 2,3-dihydrometamitron: (△) waves I₁ and I_{1a}; (◇) waves I_{1b}; (▽) waves I_{1A}. Currents corrected for variations in viscosity. Reprinted from *Journal of Electroanalytical Chemistry* **457**, 177-190 (1998).

Conclusions

Reductions of heterocyclic pesticides, containing diazine or triazine rings in aqueous media, are often complicated by adsorption. To minimize its effects concentrations lower than 0.1 mM were used and in some instances electrochemical experiments were carried out in mixtures of water with organic solvents.

All reductions in buffered aqueous media were complicated by acid-base equilibria and some of them also by a covalent addition of water or alcohols to azomethine bonds. In some instances in acidic media a chemically reversible ring-opening occurred. This investigation enabled us to find the optimum condition for polarographic determination of diazine and triazine pesticides studied (maleic hydrazide, sulfometuron methyl, hexazinone, metamitron and metribuzin). Furthermore, understanding of the role and type of chemical reaction will enable anticipation of possible matrix effects. Moreover, the oxidation-reduction and ionic processes observed, can, in principle, play a role in physiological activities of these compounds and in processes of their cleavage in a natural environment.

Acknowledgment

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