ELECTROCHEMICAL REDUCTIONS OF METHYL AZINYL KETOXIMES ON MERCURY

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Received June 29, 2000
Accepted September 8, 2000

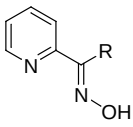
Electroreductions of hydroxyimino group of methyl hetaryl (pyridin-2-yl, pyridazin-3-yl, pyrimidin-2-yl, pyrimidin-4-yl, pyrazinyl) ketoximes on mercury electrodes were studied using dc polarography, coulometry and preparative electrolysis. Depending on pH, double-protonated, single-protonated and neutral forms of the ketoximes are transformed in a four-electron reduction to the corresponding amine. The second nitrogen in the diazine ketoximes facilitates reduction of the oxime group in comparison with methyl pyridin-2-yl ketoxime. Reducibility of the oximes correlates with the enhancement of their hydrolytic activity towards 4-nitrophenyl acetate. The reduction of the heteroaromatic ring in the diazine ketoximes proceeds at more negative potentials than the reduction of the oxime group.

Key words: Electrochemistry; Reductions; Oximes; Pyridines; Diazines; Polarography; Coulometry; Ester hydrolysis; Micellar catalysts.

Micellar catalysts for ester hydrolysis[1] attract attention of chemists due to their ability to destroy organophosphorus pesticides and chemical warfare agents. In our previous work, three series of hydrolytic catalysts were prepared and tested[2a–2c]: methyl azinyl ketoximes **1a**–**5a** (in aqueous solutions), lipophilic dodecyl azinyl ketoximes **1b**–**5b** (in micellar matrix of cetyl(trimethyl)ammonium bromide, CTAB) and their chelates with Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+}. In all these compounds, the anion of dissociated hydroxyimino group is the nucleophile attacking the ester function. Various azinyl subunits may tune the hydrolytic efficiency either directly influencing reactivity of the oxime group or indirectly, modifying the coordination ability of the whole ligand.

By kinetic measurements[2a–2c], it was proved that the hydrolytic activity of oximes **1**–**5** towards 4-nitrophenyl alkanoates strongly depends both on the type of heterocycle (number and position of the nitrogen heteroatoms) and

on the nature of the coordinated metal ion. It should be taken into account that the observed reactivity of these catalysts should increase with the acidity of the hydroxyimino group, but also with the nucleophilicity of the corresponding anion[2d]. These effects, however, are in principle contradictory, *i.e.*, the more acidic hydroxyimino group gives a higher concentration of corresponding anions which, however, are weaker nucleophiles and *vice versa*. The aim of this study is to evaluate the influence of the heterocycle on electrochemical reactivity (reducibility) of the hydroxyimino group and to correlate this reactivity with the hydrolytic efficiency towards alkanoates.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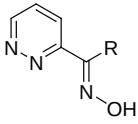
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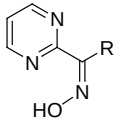
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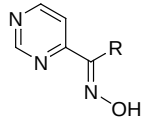
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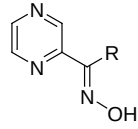
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In formulae **1-5**: **a**, R = CH_3, **b**, R = n-$C_{12}H_{25}$

Electrochemical reducibility of a molecule generally reflects the electron density (electrophilicity/nucleophilicity) on the electroactive site, and the pH dependence of the half-wave potential and limiting current give information concerning protonation-deprotonation equilibria (acidity). This paper is focused on the electrochemical investigation of uncoordinated methyl azinyl ketoximes **1a**–**5a**, *i.e.*, on the above mentioned series of ligands, namely on reduction of hydroxyimino group which is a reactive function in ester hydrolysis in the whole series and, at the same time, a coordination centre.

Electroreduction of the >C=N–OH grouping in arene aldoximes[3] and ketoximes[4] has been reported to be an overall four-electron process leading to the corresponding amino derivatives. In the case of pyridine aldoximes[5a] and ketoximes[5b,5c], differences in reduction potentials between *syn* and *anti* isomers were observed. The *syn* isomer can form an intramolecular hydrogen bridge, which makes the imino group more reducible. Regarding the influence of mutual position of the pyridyl nitrogen and the hydroxyimino group, it was found that the reduction becomes more difficult in the series pyridine-4- < pyridine-2- < pyridine-3-carbaldoxime[6a,6b,7] and, in the same order, the value of pK_a of the hydroxyimino group increases[6c]. Of the mentioned compounds **1**–**5**, only polarography of the oxime **1a** has been reported; however, without a satisfactory interpretation of the pH-depen-

dence[7]. Alkyl diazinyl ketoximes **2–5** have not been electrochemically investigated.

EXPERIMENTAL

Apparatus

^{1}H NMR spectra were recorded on a Bruker DRX 500 AVANCE and on a Varian Gemini spectrometers at 500 and 300 MHz. Chemical shifts δ are reported in ppm relative to tetramethylsilane as an internal standard, coupling constants *J* in Hz. Temperature data were uncorrected. pH measurements were performed on a Jenway 3020 pH meter. dc-Polarographic measurements were carried out with a PA4 polarographic analyzer (Laboratorní přístroje Praha) in dilute sulfuric acid (H_0 = –2.4–0, pH 0–1.2) or phosphate (pH 1.6–8.0, 11.0–12.0) and borate (pH 8.0–11.0) buffers (0.1 mol l^{-1}) under pure argon (Linde) atmosphere with an aqueous saturated calomel electrode (SCE) as a reference electrode, a Smoler-type dropping mercury electrode (Hg column height 36 cm) as a working electrode and mercury pool as an auxiliary electrode. Preparative electrolyses were carried out with a P. A. R. 173 potentiostat in 150-ml and 500-ml cells in phosphate buffers (pH 3.5 and 12.0) under argon atmosphere with mercury pool as a cathode (diameter 5.5 and 8 cm), platinum grid as an anode and SCE as a reference electrode. Sintered glass was used to separate the cathodic from the anodic compartment. Coulometric experiments were performed with a P. A. R. 263A potentiostat in 10-ml cell in phosphate buffers (pH 2.9 or 3.5) under argon atmosphere with mercury pool as a cathode, platinum sheet as an anode and SCE as a reference electrode. Sintered glass was used to separate the cathodic from the anodic compartment.

Chemicals and Solutions

Buffers were prepared from analytical grade chemicals obtained from Lachema (phosphoric acid, hydrochloric acid, sodium hydroxide, sodium hydrogenphosphate, sodium dihydrogenphosphate and sodium borate) with ionic strength 0.1. Acid solutions were prepared by dilution of sulfuric acid (96%, p.a., Lachema). Synthesis of methyl pyridin-2-yl (**1a**), methyl pyridazin-3-yl (**2a**), methyl pyrimidin-2-yl (**3a**), methyl pyrimidin-4-yl (**4a**) and methyl pyrazinyl (**5a**) ketoximes were described in a previous paper[2b]. Ketoximes were characterized by ^{1}H and ^{13}C NMR spectra and by elemental analysis[2b]. Solutions of methyl azinyl ketoximes ($5 \cdot 10^{-5}$ mol l^{-1}) were prepared in electrochemical cells by addition of 25 µl of the stock solution ($1 \cdot 10^{-2}$ mol l^{-1}) of the ketoxime to 5 ml of the buffer. Solutions were deaerated with argon before measurements.

Preparative Electroreduction of Methyl Pyridin-2-yl Ketoxime (**1a**) at pH 3.5

A solution of 0.7 g (5.14 mmol) of **1a** in 300 ml of phosphate buffer (0.5 mol l^{-1}) was reduced under stirring on mercury cathode at –1.2 V (total charge 1 990 C). pH of solution was adjusted to 10 with potassium carbonate. The resulting solution was extracted with ether. Ether was distilled off and the crude product was distilled under reduced pressure yielding 0.21 g (34%) of 1-(pyridin-2-yl)ethan-1-amine (**6**), b.p. 62 °C/800 Pa (ref.[8a] 74 °C/1 333 Pa). ^{1}H NMR ($CDCl_3$) (corresponds to ref.[8b]): 1.45 d, 3 H, *J*(CH) = 6.6 (CH_3); 2.07 s, 2 H (NH_2); 4.18 q, 1 H, *J*(CH_3) = 6.6 (CH); 7.15 dd, 1 H, *J*(5,4) = 6.6, *J*(5,6) = 4.9 (H-5);

7.30 d, 1 H, *J*(3,4) = 7.7 (H-3); 7.65 td, 1 H, *J*(4,3) = *J*(4,5) = 7.7, *J*(4,6) = 1.7 (H-4); 8.55 d, 1 H, *J*(6,5) = 4.4 (H-6). ^{1}H NMR (H_2O, phosphate buffer pH 3.5): 1.73 d, 3 H, *J*(CH) = 6.8 (CH_3); 7.54 t, 1 H, *J*(5,4) = *J*(5,6) = 5.7 (H-5); 7.60 d, 1 H, *J*(3,4) = 7.5 (H-3); 8.01 t, 1 H, *J*(4,3) = *J*(4,5) = 7.8 (H-4); 8.66 m, 1 H (H-6). ^{1}H NMR (H_2O, phosphate buffer pH 10.0): 1.29 d, 3 H, *J*(CH) = 6.7 (CH_3); 7.24 t, 1 H, *J*(5,4) = *J*(5,6) = 5.4 (H-5); 7.36 d, 1 H, *J*(3,4) = 7.9 (H-3); 7.76 t, 1 H, *J*(4,3) = *J*(4,5) = 7.8 (H-4); 8.34 m, 1 H (H-6).

Preparative Electroreduction of Methyl Pyridin-2-yl Ketoxime (**1a**) at pH 12.0

A solution of 0.1 g (0.73 mmol) of **1a** in 70 ml of phosphate buffer was reduced under stirring at –1.7 V (total charge 256 C). The crude product was characterized as amine **6** by ^{1}H NMR in water (pH 10.0) and in $CDCl_3$ solutions.

RESULTS AND DISCUSSION

Compounds **1**, **2**, **4** and **5** are *E*-isomers, only the ligand **3** is a *Z*-isomer.

*Reduction of Methyl Pyridin-2-yl Ketoxime (**1a**)*

The electroreduction of (*E*)-methyl pyridin-2-yl ketoxime (**1a**) in the pH range from –2.3 to 12 is manifested by three successively appearing different four-electron waves (Figs 1a, 1b). In acid and neutral media, the ketoxime is reduced in the most positive wave A, the half-wave potential of which is first pH-independent (up to pH 2.0) and then pH-dependent between pH 2.0–8.0 (shifted by 100 mV/pH to more negative potentials). The

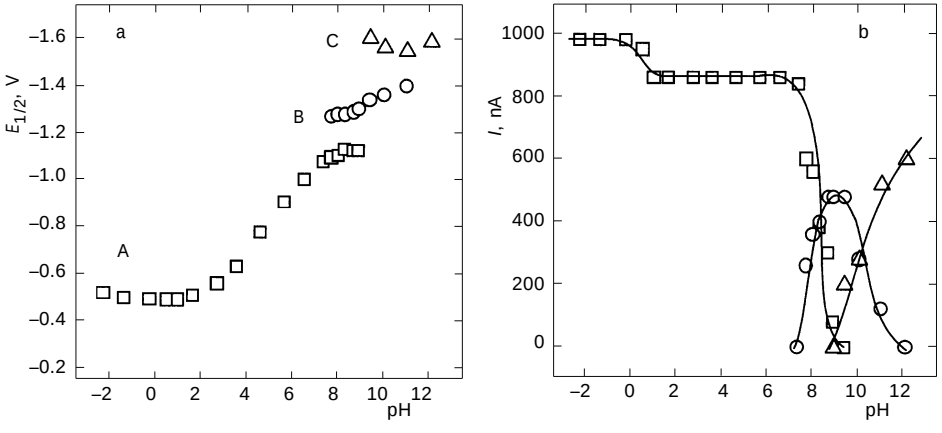
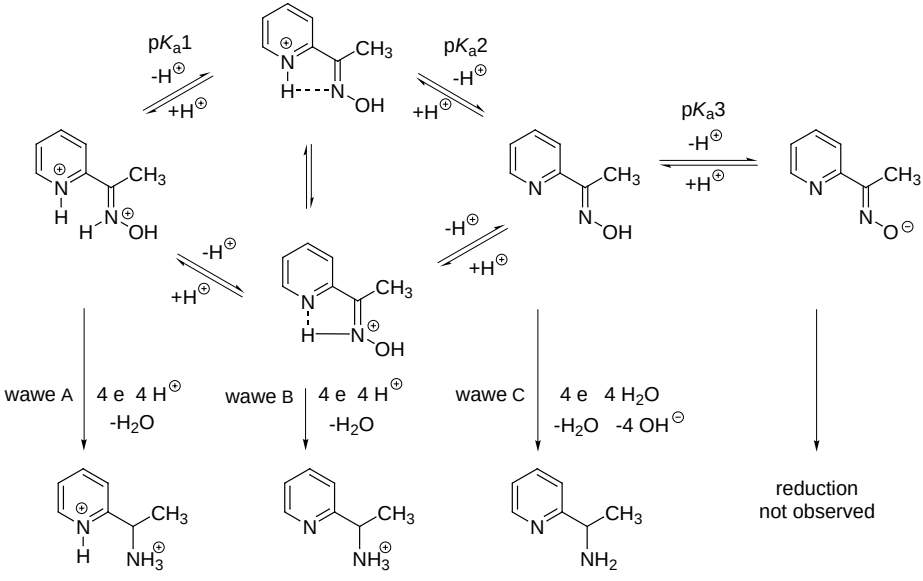


FIG. 1
pH dependence of half-wave potential (a) and limiting current (b) of reduction waves of the hydroxyimino group in **1a**. Different symbols indicate reduction of the double-protonated (❑, wave A), single-protonated (○, wave B) and neutral (Δ, wave C) form of the oxime

limiting current corresponding to a four-electron process (checked by comparison with standard substances: benzophenone and 3-nitrobenzoic acid) is constant in the pH range 0.5–7.5. The higher limiting current in strongly acid solutions ($[H_2SO_4] > 1$ mol l^{-1}) has not been explained. At pH > 7.5, the height of wave A decreases to zero with increasing pH. The limiting current *vs* pH plot (Fig. 1b) has a shape of a dissociation curve with an inflexion point (so called polarographic pK' value) at pH 8. At pH > 7.5, the wave A is gradually replaced by a more negative wave B with the virtually pH-independent total wave height (*i.e.*, together with wave A). The half-wave potential of wave B is also pH-dependent (with a slope of 70 mV/pH between pH 7–11). At pH > 9.5, the height of wave B decreases to zero and with increasing pH is gradually replaced by the most negative wave C, the $E_{1/2}$ of which is pH-independent.

Thus, three forms of ketoxime **1a** are reduced (Scheme 1). Wave A corresponds to the reduction of the species, protonated both on the oxime and heterocyclic nitrogens. The pH-independent part corresponds to the situation when the double-protonated form prevails in solution, *i.e.* under pK_a1.



SCHEME 1

The ascending part of the dependence represents the situation when the solution contains mainly the single-protonated form and the reduction of double-protonated species depends on the antecedent acid–base equilibria.

At pH > 7.5, the reduction becomes kinetically controlled due to slow protonation pre-equilibria (characterized by the p*K*′ value); wave A decreases and a new wave B appears corresponding to reduction of the single-protonated species. In the bulk of the solution, the form protonated on heterocyclic nitrogen prevails; however, oximes are more easily reduced in the form protonated on the oxime nitrogen (fast acid–base equilibrium enables sufficient production of reducible species). Since wave B exists at pH higher than[9] the pK_a2 = 4.0, even at these pH values preprotonation takes place, the wave is pH-dependent and at pH > 9.5 is also kinetically controlled. The most negative pH-independent wave C corresponds to the direct reduction of the neutral unprotonated molecule of the ketoxime. Since further dissociation equilibria of the oxime hydrogen proceeds at very high pH (pK_a3 = 11.1, ref.[2b]), reduction of the anionic species was not observed.

In the literature dealing with reduction of phenyl pyridin-2-yl ketoxime and pyridine-2-carbaldoxime, it is reported that the resulting amines undergo, at very negative potentials, another two-electron reduction[5c,6b] representing reductive splitting of the amino group. This deamination was not observed with our compounds, most probably due to even more difficult reduction caused by the positive inductive effect of the methyl group. From a comparison of reduction potentials at pH 4 and substituent constants σ_X^* (ref.[10]) of phenyl pyridin-2-yl ketoxime (–0.577 V (ref.[5b]), σ_X^* (C_6H_5) + 0.60) and pyridine-2-carbaldoxime (–0.645 V (ref.[6b]), σ_X^* (H) + 0.49) with those of **1a** (–0.700 V, σ_X^* (CH_3) + 0.00), it is evident that the reduction potential of the oxime grouping generally reflects the influence of neighbouring substituents.

A similar $E_{1/2}$ *vs* pH dependence was reported by Gardner[4a] for the reduction of acetophenone oxime and benzophenone oxime. In his case, however, there is no nitrogen heteroatom to be protonated. The situation is thus simpler and the only preprotonation equilibria involve the oxime nitrogens. On the observed pH dependence, below pH 2, pH-independent reduction of the protonated species occurs. At higher pH, the same reduction is controlled by preprotonation of the oxime.

*Reductions of Diazine Ketoximes **2a**–**5a***

Whereas oxime **1a** has only one reducible group, electroreduction of diazine ketoximes **2a**–**5a** is more complicated due to the fact that the heterocycles are activated by the presence of second nitrogen heteroatom. The heterocyclic azomethine bonds are thus reducible but at more negative potentials than the oxime group. In our study, main attention has been

paid only to the reduction of the oxime grouping, which is important from the catalytical point of view.

The obtained pH dependencies (both of half-wave potentials and of limiting currents) of **2a**–**5a** follow analogous patterns to those of **1a** (Figs 2–5): waves A correspond to reduction of double-protonated species, waves B to

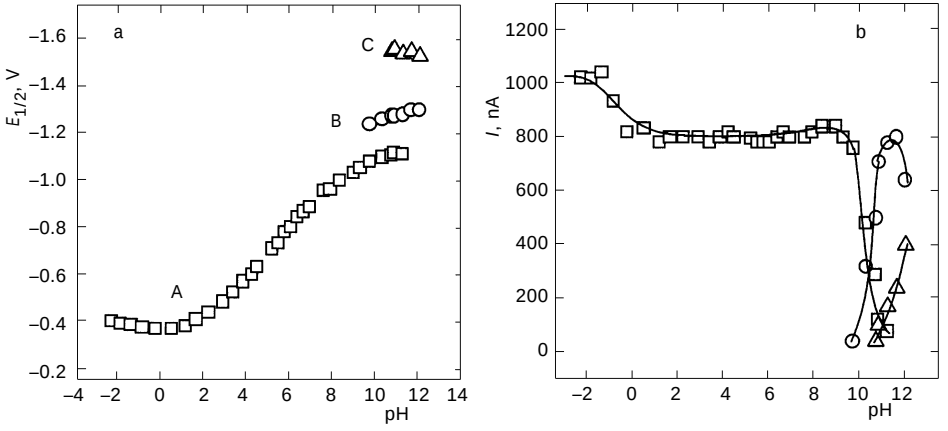


FIG. 2

pH dependence of half-wave potential (a) and limiting current (b) of reduction waves of the hydroxyimino group in **2a**. Different symbols indicate reduction of the double-protonated (❑, wave A), single-protonated (○, wave B) and neutral (Δ, wave C) form of the oxime

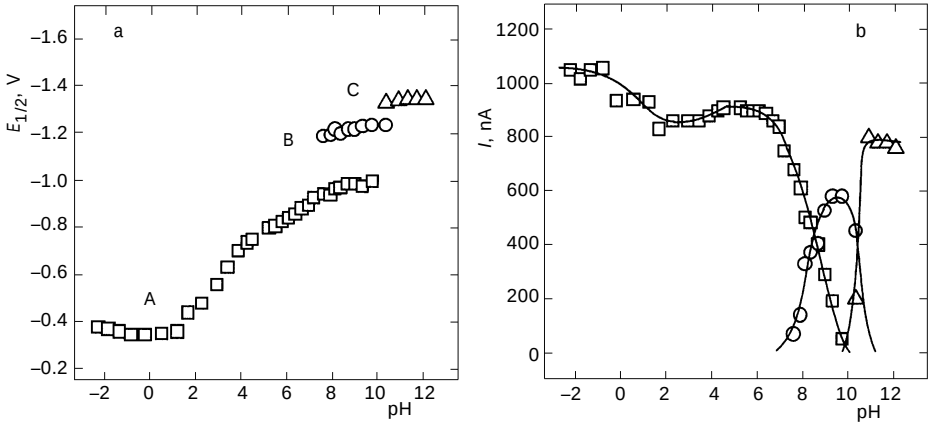


FIG. 3

pH dependence of half-wave potential (a) and limiting current (b) of reduction waves of the hydroxyimino group in **3a**. Different symbols indicate reduction of the double-protonated (❑, wave A), single-protonated (○, wave B) and neutral (Δ, wave C) form of the oxime

reduction of single-protonated species and waves C, the most negative and pH-independent, reflect reduction of unprotonated, neutral oximes.

Electrochemical data are summarised in Table I together with pK_a values of the oxime groups and their apparent catalytic activities. From Table I it is evident that the second nitrogen in the heterocycle facilitates the reduction

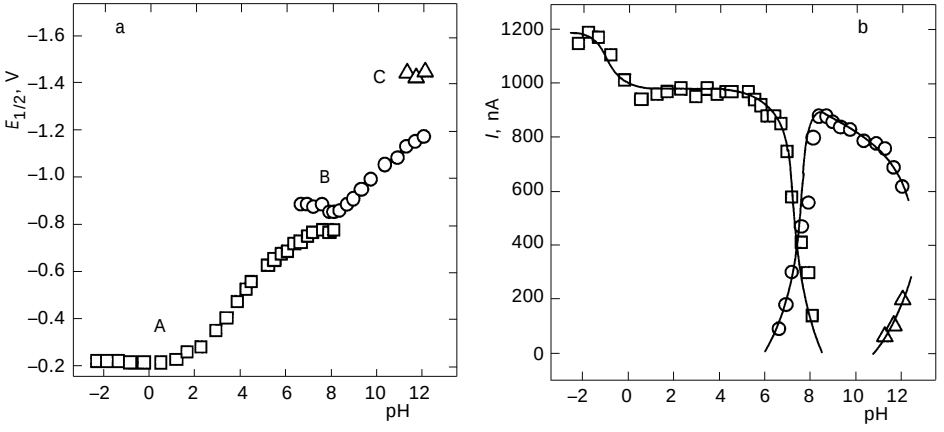


FIG. 4

pH dependence of half-wave potential (a) and limiting current (b) of reduction waves of the hydroxyimino group in **4a**. Different symbols indicate reduction of the double-protonated (❑, wave A), single-protonated (○, wave B) and neutral (Δ, wave C) form of the oxime

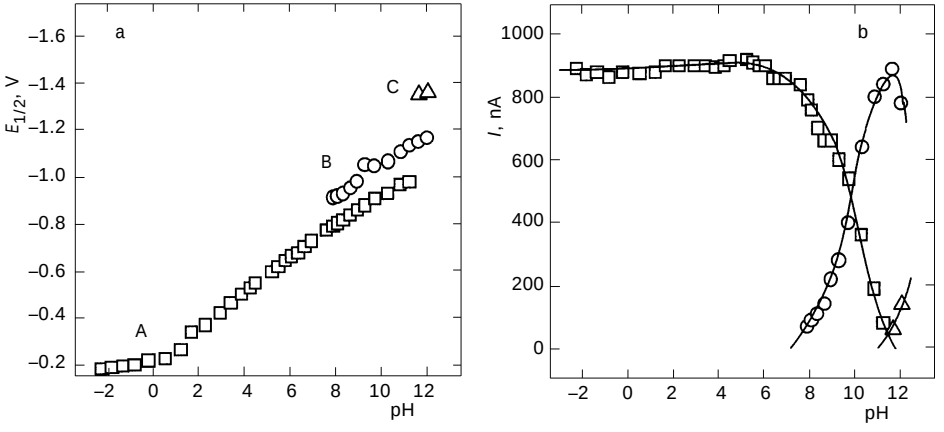


FIG. 5

pH dependence of half-wave potential (a) and limiting current (b) of reduction waves of the hydroxyimino group in **5a**. Different symbols indicate reduction of the double-protonated (❑, wave A), single-protonated (○, wave B) and neutral (Δ, wave C) form of the oxime

of the oxime grouping, which manifests itself by a decrease in the reduction potential. Simultaneously, the pK_a values (including pK_a3) become lower (corresponding to higher acidity) and, consequently, the concentration of the nucleophilic dissociated oxime group is enhanced. These facts correlate with increasing catalytic activity of the corresponding ketoxime (Fig. 6). From these results it follows that for the hydrolytic activity of ox-

TABLE I
Comparison of electrochemical data with pK_a values and hydrolytic activity of ketoximes **1a**–**5a**

Oxime	$E_{1/2}$[a], V[b]	pK_a1[c]	pK_a3 (ref.[2b])	Hydrolytic activity[d]
1a	–0.575	2.0	11.1	1
2a	–0.485	2.0	10.6	1.52
3a	–0.560	1.0	10.8	1.12
4a	–0.350	1.8	10.3	2.58
5a	–0.420	0.6	10.9	1.13

[a] Values for pH 2.9 (the same order of values has been found for the whole acid and neutral region, *i.e.* from pH –2 to 7). [b] *Versus* SCE. [c] Estimated from $E_{1/2}$ *vs* pH plots. [d] Hydrolytic activity towards 4-nitrophenyl acetate[2b] in neutral media (relative to the value for compound **1**).

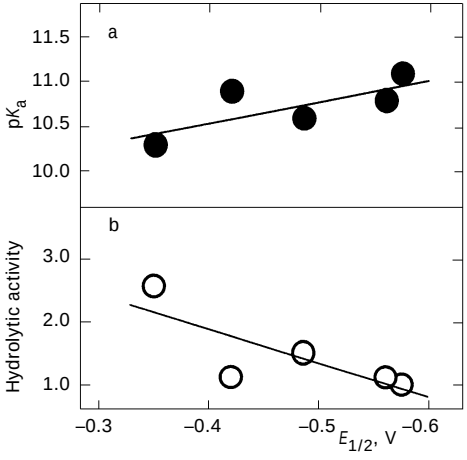


FIG. 6
Correlation of pK_a3 of the hydroxyimino group (a) and of hydrolytic activity (relative values) towards 4-nitrophenyl acetate (b) for ketoximes **1a**–**5a** with half-wave potential at pH 2.9

imes **1**–**5**, the influence of the azine on the concentration of the anion formed by dissociation of hydroxyimino group is more significant than the influence of the azine on its nucleophilicity.

The pK_a1 values (reported in Table I) of the double-protonated species correspond to the pH values of the intersection of two linear parts of the $E_{1/2}$ = *f*(pH) plot in acidic media (change from the pH-independent situation to a linear pH dependence). The pK_a2 values of the single-protonated species cannot be obtained from polarographic data; however, these values are probably very close to those of pK_a1 values. It is evident that during the reduction at pH 4–8, a two-step preprotonation reaction takes place. This explains some distortion of the $E_{1/2}$ *vs* pH plots corresponding to waves A (and partly also to waves B) in the mentioned pH region. For the same reason, the decrease in the *I*(A) = *f*(pH) plot is less steeper (over several units of pH) impeding the evaluation of apparent polarographic pK' values (Figs 2–5).

In contrast to oxime **1a,** diazine ketoximes afford two possibilities of protonation in the rings. From the obtained results it is not possible to decide unambiguously which heterocyclic nitrogen is preferentially protonated. Semiempirical quantum chemical calculations (PM3, ref.[11]) of electron charges on ring and oxime nitrogen atoms (Table II) make possible to anticipate that in all diazines, the preferentially protonated atom is the ring nitrogen farther from the oxime group with an exception of **3** where both ring nitrogens are close to oxime group. The problem of the protonation site in the heterocycle is, however, complicated by the intra-

TABLE II
Atomic charges on heterocyclic and oxime nitrogens of ketoximes calculated using PM3 method

Ketoxime	=N–OH	Heterocycles	
		N(1)[a]	N(2)
1a	–0.021	–0.058	–
2a	–0.021	–0.006	–0.025
3a	–0.003	–0.088	–0.088
4a	–0.011	–0.097	–0.115
5a	–0.016	–0.022	–0.044

[a] Nitrogen closer to the (1-hydroxyimino)ethyl substituent.

molecular hydrogen bridge between the oxime nitrogen and the α-nitrogen in the ring.

As for the reduction of the diazine heterocycles that occurs at more negative potentials, compound **2a** exhibits two two-electron waves that are pH-dependent. This pattern is very similar to the behaviour of 1,2,4-triazine derivatives[12], corresponding most probably to stepwise reduction of 1,6- and 2,3-azomethine bonds. Compound **3a** is further reduced with one four-electron wave which splits at pH 8 into two two-electron waves. The reduced compounds **4a** and **5a** exhibit only one four-electron wave in the whole pH range, the pH dependence of which ($E_{1/2}$ = *f*(pH)) changes its slope at pH 8. More detailed study of these electroreductions was not done.

Coulometry and Preparative Electrolyses

To confirm the identity of the product and the number of electrons consumed during the reduction, preparative electrolyses and coulometry of **1a** at two different pH values (phosphate buffers pH 3.5 and pH 12.0) on a mercury pool electrode were performed. At both pH, a four-electron process was found (Table III) and the only isolated product was 1-(pyridin-2-yl)ethan-1-amine (**6**). Immediately after the electrolysis the solution was analysed by ^{1}H NMR spectroscopy in aqueous electrolyte[13] confirming that only the corresponding amine **6** was formed.

Similarly, preparative electrolyses of substances **2a–5a** accompanied by coulometric measurements were performed in a semipreparative electrolytic

TABLE III
Results of coulometry with ketoximes

Ketoxime	pH	*E*, V	*N*, mmol	*Q*, C	*n*, F mol^{-1}
1a	3.5	–1.2	5.14	1 990	4.03
1a	12.0	–1.7	0.73	256	3.66
2a	2.9	–0.80	0.104	36.1	3.62
3a	2.9	–0.95	0.071	27.8	4.07
4a	3.5	–0.95	0.063	22.4	3.70
5a	3.5	–0.95	0.097	35.7	3.84

cell[14] on a mercury pool electrode. The reduction potential was set up on the limiting current of the first wave. Since the polarographic wave should not generally reflect the situation on a large electrode[15], a polarization curve has been constructed point by point for the mercury pool electrode before every experiment in order to assure that only the first reduction would take place. During the electroreduction, the amount of remaining starting diazine was checked polarographically. In all experiments, a four-electron process was found (Table III). By analogy to the electroreduction of **1a**, the corresponding amine might be the main product.

The authors thank the Grant Agency of the Czech Republic for financial support of this work (grants No. 203/97/0805 and No. 203/99/0763).

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