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Electrochemical Reduction of the Imidazolinone Herbicide Imazamethabenz Acid on Mercury and Carbon

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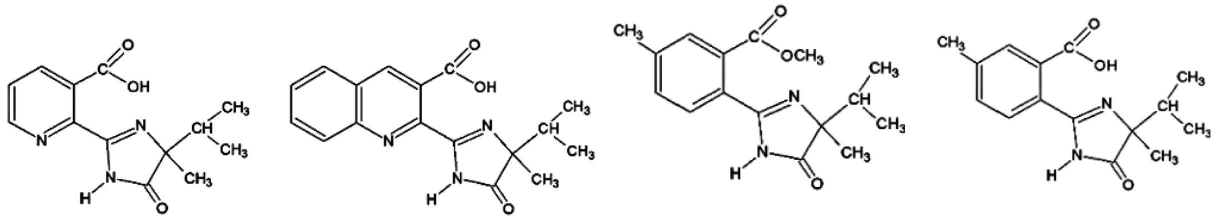
This paper presents polarographic and voltammetric studies of the reduction of the herbicide imazamethabenz acid on mercury electrodes. The electrochemical studies were performed from strongly acidic media (0.1 to 2.7 M H_2SO_4) to pH range 12. The overall reduction process involves the uptake of two electrons. The results obtained show that three species are reduced related via acid-base equilibria, being the reducible group the imidazolinone ring. In strongly acidic media ($pH<pK_a$), the reaction mechanism proposed is the reduction of the protonated herbicide by an irreversible process, being the r.d.s. the second electron transfer. At $pH>pK_a$ two H^+ ions are uptaken prior the reduction. In the reduction of the carboxylate unprotonated form of the herbicide, the second electron transfer becomes reversible or quasi-reversible. The possibility of the reductive degradation in natural waters is discussed.

Keywords: Reduction mechanisms, imazamethabenz acid, imidazolinone herbicides, electrode kinetics.

1. INTRODUCTION

Imidazolinone herbicides, such as imazapyr, imazethapyr, imazaquin or imazamethabenz, have low toxicity for humans and can constitute an alternative to chlorinated triazine herbicides, simazine, atrazine, propazine, etc., or to phenoxy herbicides such as 2,4-D and 2,4,5-T. The reductions of imazapyr, imazethapyr and imazaquin in the whole pH range (2.7 M H_2SO_4 to pH 13) have been studied by polarography [1]. The signals observed in differential pulse (DP) polarography were assigned to the reduction of the pyridinic (or quinolinic) and the imidazolinone rings (see scheme below). The results suggested that the peaks appearing at more negative potentials could be related to the heterocyclic ring reduction, being the assignation of the peaks appearing at less negative potentials more difficult.



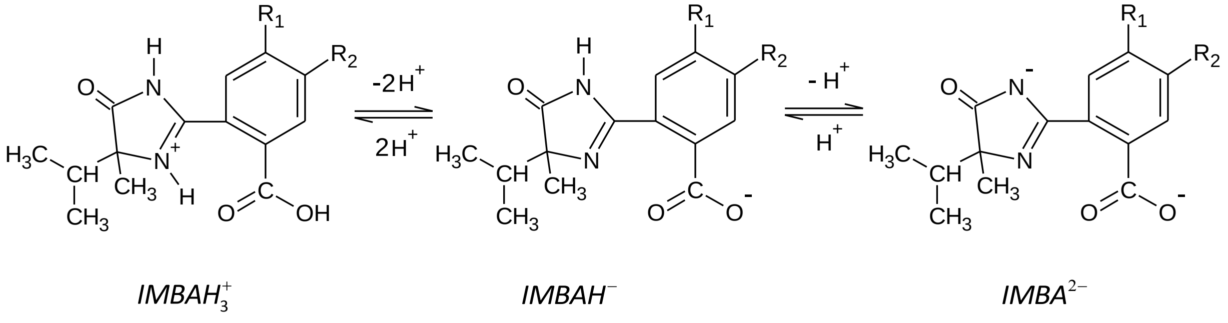
Scheme I. Structures of imazapyr, imazaquin, imazamethabenz methyl and imazamethabenz acid (from left to right).

From scheme I it follows that the difference between imazamethabenz (acid or methyl) and the rest of imidazolinones resides in the aromatic part of the molecule, this being a substituted benzoic acid for imazamethabenz, or a nitrogenated heterocycle for the rest of herbicides. Benzoic acids and their esters are not electroreduced in aqueous media and thus the electrochemical behaviour of imazamethabenz acid must be due to the reduction of the imidazolinone part of the molecule. The electrochemical behaviour of the heterocyclic imidazolinone herbicides can be better understood because the imidazolinone part of all the molecules is the same.

In a previous work polarographic and voltammetric studies were made on the reduction of imazamethabenz methyl (This compound must have a less complicated behaviour than imazamethabenz acid due to the absence of the carboxylic group) on mercury and carbon electrodes [2]. Two species, related via an acid-base equilibrium, and having very close reduction potentials are reduced. The results obtained with a glassy carbon electrode were very similar to those observed on mercury electrodes. At $pH<pK_a$ protonated herbicide is reduced by an electrochemical-chemical-electrochemical process (ECE), being the r.d.s. the second electron transfer. At $pH>pK_a$ the neutral form of the herbicide is reduced and the second electron transfer becomes reversible or quasi-reversible. In basic media, the species reduced is the deprotonated imazamethabenz methyl and the r.d.s. is the second electron transfer.

No references can be found about the electrochemical behaviour of imazamethabenz acid. So, the aim of this paper was to investigate the reduction pathways of this herbicide on mercury electrodes to contribute to the elucidation of the reduction mechanisms of the heterocyclic imidazolinone herbicides. In this context, electrochemistry is being used in last years to explore the quantitative determination of herbicides [3, 4] or event its effect on DNA repair [5].

The protonation state of the species in solution must be knowledged for the elucidation of the reduction mechanisms. Values of $pK_1= pK_2=3.3\pm0.1$ corresponding to the protonation of the imidazolinone nitrogen and the dissociation of the carboxylic group, and $pK_3=9.6\pm0.2$ corresponding to the dissociation equilibrium of the imidazolinone nitrogen in alpha position with respect to the carbonyl group, were determined in the authors' laboratory [6].



Scheme II. Protonation-dissociation reactions of Imazamethabenz Acid

2. EXPERIMENTAL

In all cases, Merck analytical grade reagents were used with the exception of imazamethabenz methyl which was from Riedel de Haën (analytical standard). Imazamethabenz acid was prepared by alkaline hydrolysis of imazamethabenz methyl as follows [7]: 10 mL of 2M NaOH solution were added to 500 mg of IMBM and the suspension was stirred at room temperature until clear (about 3 h). The solution was washed with chloroform, and concentrated HCl was added until precipitation of the acid that was filtered and re-crystallized from ethanol.

All other reactants were used without further purification. The working concentration of reactant was $2x10^{-4}$ *M*, for polarographic measurements and $1x10^{-3}$ *M*, for voltammetric measurements, with the exception of the experiments in which the influence of this variable was studied. Solutions of either sulfuric acid, for pH<2, 0.05 *M* in both acetic and phosphoric acids for 2<pH<8 or 0.05 *M* in both sodium carbonate and phosphoric acid for pH>8 were used as supporting electrolytes. The ionic strength was adjusted to 0.3 M with NaCl. The pH was adjusted with solid NaOH. All potentials were measured against the $Ag/AgCl/KCl_{sat}$ electrode. Solutions were purged with purified nitrogen and the temperature was kept at 25±0.1 ºC. The aqueous solutions were prepared using ultrapure water type I (resistivity 18.2 MΩ.cm at 25ºC) obtained by an ultrapure water system Millipore Simplicity®.

A BAS 100 workstation was used for the voltammetric and polarographic measurements. The mercury working electrode was a BAS MF-9024 controlled growth electrode, with an area of $6.70x10^{-3}$ cm^2. Triply distilled mercury was used. The glassy carbon electrode was from IJCambria having a geometrical area of 38.5 mm^2.

3. RESULTS AND DISCUSSION

In the pH range studied, imazamethabenz acid showed two reduction waves in tast polarography, the polarograms being distorted at pH<4 due to the appearance of a polarographic maximum. The limiting current, i_L, of the first wave (that is, the wave appearing at less negative potentials) is roughly pH-independent at pH<4.5, decreasing above this pH value and disappearing at c.a. pH=8. The value of i_L corresponded to a two-electron process as was confirmed by comparing i_L with the value corresponding to the reduction of imazamethabenz methyl [2].

The logarithmic analyses, made in the form of E vs. log $[i/(i_L–i)]$ plots, were roughly linear with slopes of c.a. –33 to –37 mV per decade at pH<4 and pH>8, respectively. In the pH range 4-8 the slope changed gradually, reaching a value of –56 mV per decade at pH 3.5.

Scheme II shows that below pH 3.3 the protonated species is that present in the solution, in the pH range 3.4-9.4, the species in solution is the imazamethabenz-carboxylate and above this last pH value the solution contains the dianionic form.

Since there is no evidence of the occurrence two waves at $pK_1<pH<pK_3$, the reduction potentials of the two species involved in the first acid-base reaction (involving two H^+ ions) must be very close. To separate the contributions of such processes, DP polarography is commonly used. In fact, the conclusions on the electrode kinetics of the reduction processes given in this paper are mainly supported by the DP polarographic (and voltammetric) results. Some DP polarograms are shown in fig. 1.

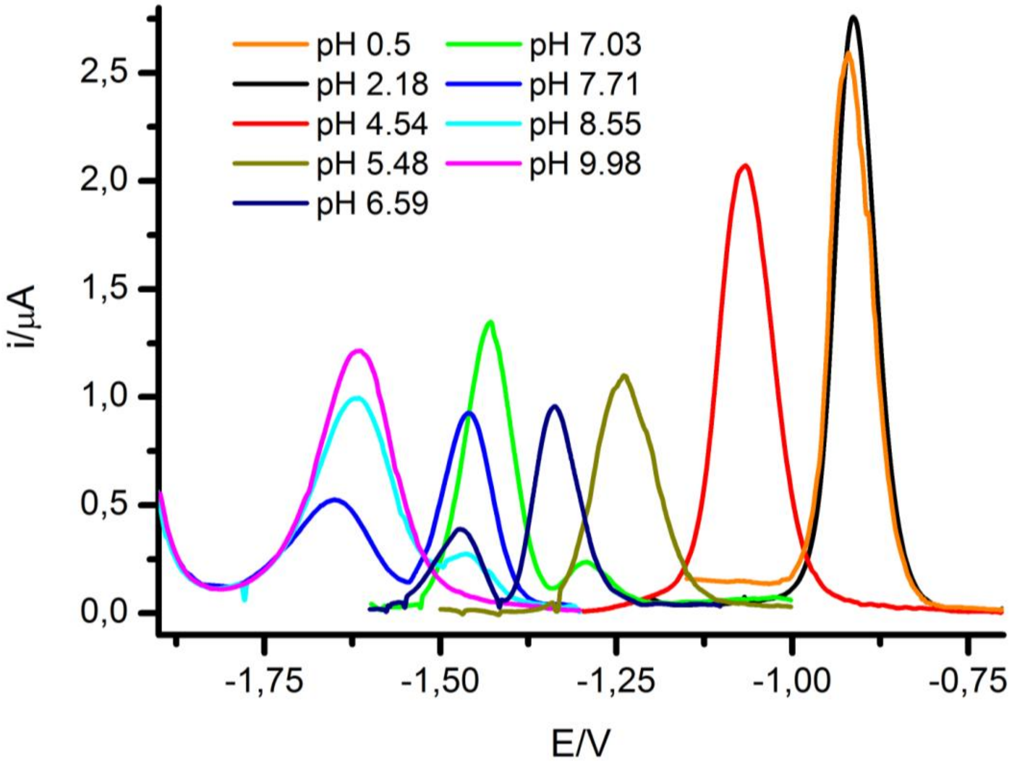


Figure 1. Mercury electrode. DP polarograms of $2x10^{-4}$ M Imazamethabenz Acid. Sample width 20 ms; pulse width 50 ms; pulse amplitude 20 mV; dropping time 1 s. pH values are given in the figure.

The analysis of the DP polarograms was performed by using the following equation corresponding to first-order processes [8]:

$$I = 4I_P \frac{L}{(1+L)^2} \tag{1}$$

where $I=\Delta i/\Delta E$, $L=\exp[-(E-E_P)/b]$, I_P and E_P being the peak intensity and the peak potential, respectively, I is the dc current and b is a parameter which has the same value as the slope of the dc logarithmic analysis. E_P and I_P values are related to those of $E_{1/2}$ and i_L [8, 9].

As can be seen in fig. 2, the peak intensity varied from a constant value, in strongly acidic media, to another value, in the pH range 6-7, showing a minimum at an intermediate pH close to 5. The experimental b value obtained from the half-width of the peak experiences a “reverse” variation, i.e. shows a maximum at the pH values where the peak intensity shows the minimum (as the logarithmic analysis slopes in dc polarography do). This is characteristic of the reduction of two species related *via* a protonation equilibrium and having very close reduction potentials [10].

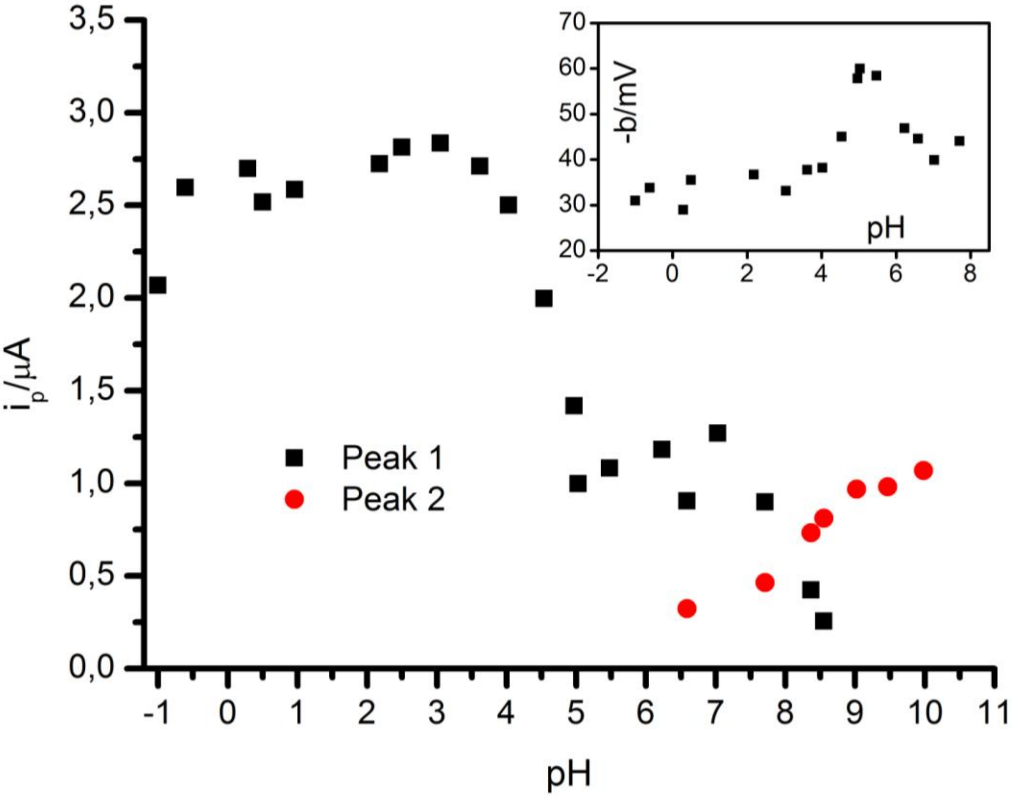


Figure 2. Mercury electrode. DP polarography of $2x10^{-4}$ M Imazamethabenz Acid. Dependence with pH of peak currents and b values (inset)

Since the b values of both peaks are different, the comparison of their peak currents is not adequate. In the derivation of equation 1, it was made the approximation that the DP intensity is equal to the first derivative of the dc current with respect to the potential [8, 11]. The validity of this assumption increases as the pulse amplitude decreases and is valid for pulse amplitudes lower than 20-25 mV as is the actual case [9]. So, the dc current can be obtained by integration of equation 1. Thus, the comparison of the DP intensities must be made through the peak area, as shown in fig. 3.

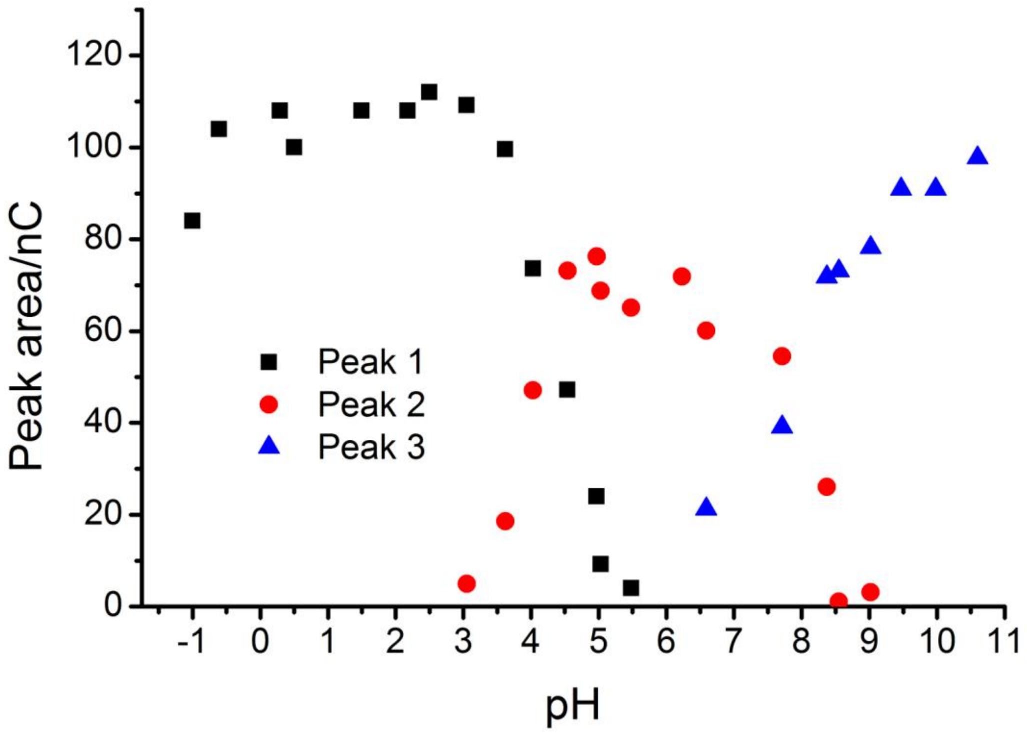


Figure 3. Mercury electrode. $2x10^{-4}$ M Imazamethabenz Acid. Dependence of the peak areas of DP polarograms with the medium pH.

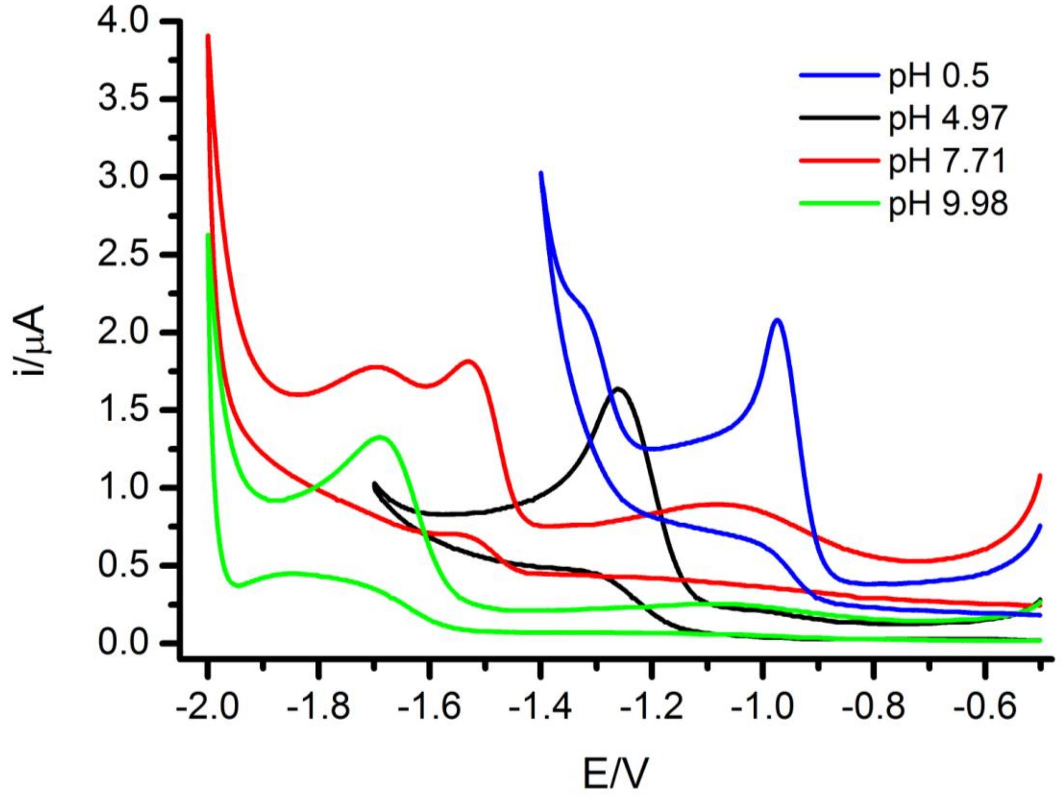


Figure 4. Mercury electrode. Cyclic voltammograms of $2x10^{-4}$ M Imazamethabenz acid at 0.1 $V \cdot s^{-1}$. pH values are given in the figure.

As can be seen, the peaks are complementary, i.e., as the one peak decreases, other peak increases, the shape of the graph resembling an acid-base dissociation curve, having pK values at c.a. pH=3.5 and pH=8.8, that is, at the pK_a values of imazamethabenz Acid. This means that, at the potentials corresponding to the limiting currents, and in the pH range where these limiting currents vary, the rate of the reduction processes are controlled by the protonation/acid dissociation reactions, each reduction process being two-electron. Thus, the protonated form of the imazamethabenz acid is that responsible for the appearance of peak 1, the imazamethabenz-carboxylate for peak 2, the dianionic form for peak 3.

The slopes of the E_P vs. pH plots obtained from the deconvolution of the DP polarograms were 0 and –85 mV per pH unit for the first peak at pH<3 and pH>3.5, respectively; for the peak 2 this slope was –69 mV per pH unit and the peak potential of peak 3 was roughly pH-independent above pH 7.5. These values, together the values of the b parameter indicate that zero and two H^+ ions take part in the electrochemical processes prior or in the rate-determining step, r.d.s., in the abovementioned pH ranges for peak 1, one H^+ ion for peak 2 and zero H^+ ions for peak 3.

The overall reduction process is irreversible, since no re-oxidation peaks were observed in the reverse scans of the linear-sweep cyclic voltammograms (fig. 4).

Convolution voltammetry [12-19] was used to analyze the direct scans of the voltammograms. S-shaped curves were so obtained having a limiting value J_L independent of the mechanism of the electrochemical reaction. Diagnostic criteria can be established using logarithmic analyses based on the equation [11-19]:

$$E = E1/2 + b \ln[f(I, J)] \qquad (2)$$

where f(I, J) is a function that depends on the actual mechanism of the electrochemical reaction, and b is the so-called “logarithmic analysis slope” with the same meaning as the b parameter in DP polarography.

f(I, J) corresponding to irreversible, E_i, or EC processes was used for the analysis of the first voltammetric peak and the b values obtained varied with the pH in a similar way as shown in the inset of figure 2 for DP polarography. In addition, J_L values depended on the pH in a similar way as the DP peak area and the variations of $E_{1/2}$ values were roughly the same as the dc half wave potentials and experimental DP peak potentials.

The results obtained by using a glassy carbon electrode were very similar to those described above for the mercury electrode.

No re-oxidation peaks were observed in the reverse scans, as can be appreciated in figure 5, and both the electrochemical parameters and their variations were similar to those obtained for mercury. The reduction peaks appeared at c.a. 110-160 mV more negative than in the mercury electrode and the absolute values of b were slightly greater. In addition, the dependence of the peak current with the scan rate indicates that the adsorption of the reactant on the electrode is involved in the electrochemical process.

Finally, the characteristics of the i-E curves and their dependencies with the experimental parameters indicate that the reduction processes are essentially the same as in mercury electrodes.

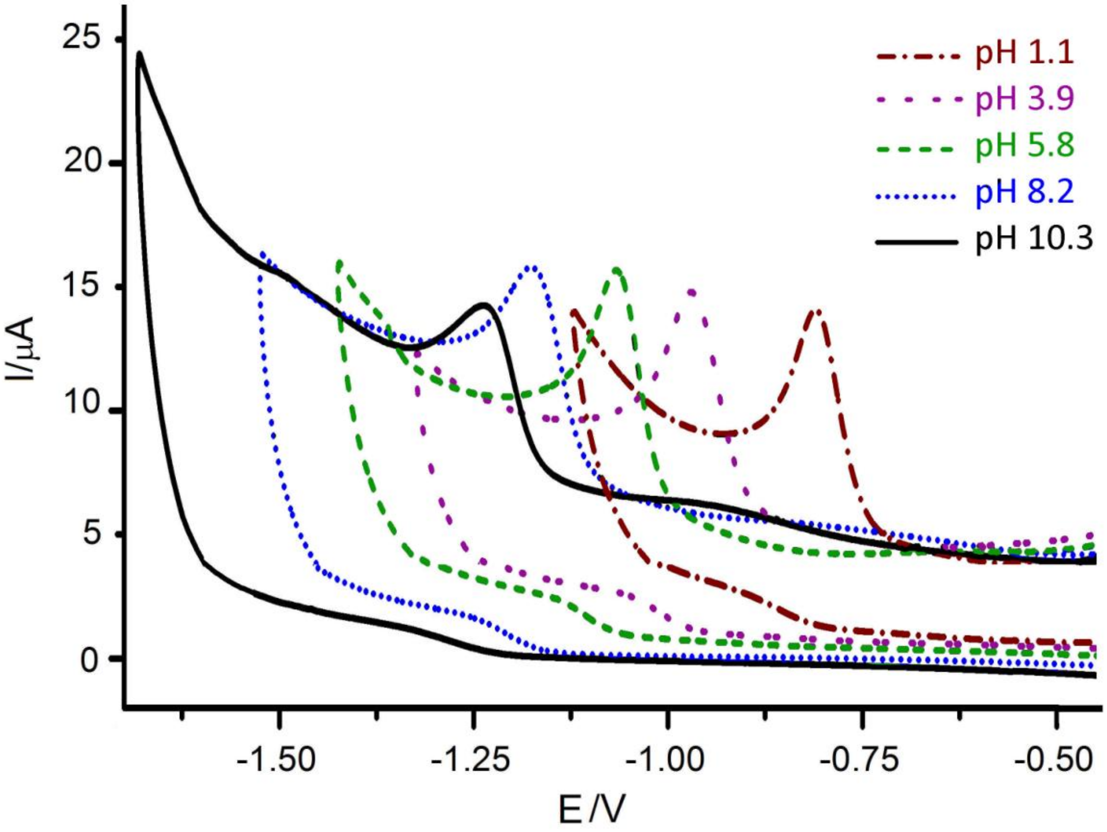


Figure 5. Glassy carbon electrode. Cyclic voltammograms of 2x10^{-4} M imazamethabenz acid at 0.1 V·s^{-1}. pH values are given in the figure

As in the case of imazamethabenz methyl [2] the only reducible group in the molecule, in the accessible potential window, is the imidazolinone ring. Taking into account all the abovementioned results and conclusions, and the results reported in references [2] and [6], the following reduction scheme is proposed for the first peak at pH<3.3:

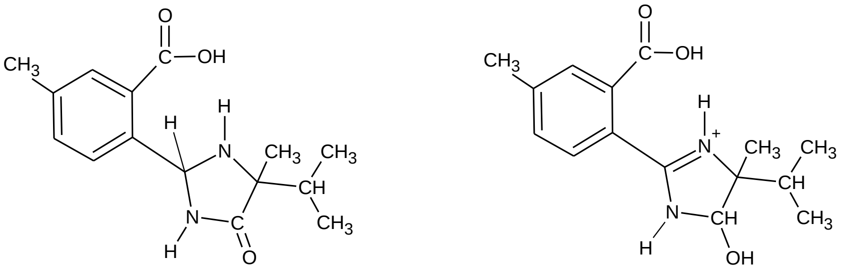
$$IMBAH_3^+ + e^- \rightleftharpoons R^\bullet$$

$$R^\bullet + e^- \xrightleftharpoons{r.d.s.} R^-$$

$$R^- + 2H^+ \rightleftharpoons RH_2$$

From the pK$_a$ value of the amidinium ion it follows that imazamethabenz acid is not acidic enough to protonate the carbonyl and the experimental results show that no H$^+$ ions are taken prior or in the r.d.s. This behaviour is different from that corresponding to the reduction of the same species for imazamethabenz methyl [2]. In the case of the acid, the species obtained after the first electron transfer is a uncharged radical that is subsequentely reduced in the r.d.s., the anion obtained in this step being protonated in the following step, while in the case of the methyl derivative the radical is protonated prior the second electron transfer.

In the above squeme, RH_2 is the product of the two-electron reduction of the protonated IMBA, either in the imine or in the carbonyl group of the imidazolinone ring:



Scheme III. Possible structures of the reduction products in acidic media

No evidences are given in the literature on the reduction of the C=N bonds of imidazolines, even under the protonated form of imminium ion. The immine derivatives that are reduced on mercury electrodes must be strongly activated by conjugation with other double bonds in the heterocyclic ring [8]. Other reducible immine derivatives are non-cyclic derivatives having the nitrogen attached an H atom or a –OH group [20, 21]. Thus, if the benzoic rest adjacent to the C=N bond is activating enough, the immine is reduced. In the opposite case, the ring carbonyl group should be reduced.

At pH values higher than 3.3 (pK_a) the species present in the solution is the unprotonated imazamethabenz carboxylate, $IMBAH^-$. Thus, a double protonation, as shown in scheme II, must precede the above scheme, and so, the electrochemical reaction order with respect to the H^+ ion is increased to 2, according to the experimental results.

At the potentials corresponding to the second peak, the molecule reduced at the electrode is the same as the molecule in solution, i.e., $IMBAH^-$. The electrochemical parameters indicate that the second electron transfer becomes reversible or quasi-reversible and that one H^+ ions is involved in the reaction prior or in the r.d.s. So, for the peak 2, the following scheme is proposed:

$$IMBAH^- + e^- \rightleftharpoons P^{\bullet 2-}$$

$$P^{\bullet 2-} + H^+ + e^- \xrightleftharpoons{r.d.s.} PH^{2-}$$

$$PH^{2-} + H^+ \rightleftharpoons PH_2^-$$

Where PH_2^- is the carboxylate form of RH_2.

This scheme is essentially the same as that given for the second peak in the reduction of imazamethabenz methyl [2] though the uptake of the second H^+ ion must take place after the r.d.s.

The electrochemical parameters corresponding to the peak 3 in basic media indicate that the species reduced is $IMBA^{2-}$, but the type of both the electron transfers and the r.d.s. is not clear. So, the results indicate that the first electron transfer must be irreversible or quasi-reversible and that the H^+ ions are not involved prior or in the r.d.s. So, it seems plausible that $IMBA^{2-}$ is reduced to a strongly basic trianion that is capable of take an H^+ ion from a H_2O molecule, this being the r.d.s. This behavior is again similar to that of imazamethabenz methyl.

The deactivation in the natural environment of imidazolinone herbicides imazamethabenz acid and methyl (as for other herbicides) occurs generally via oxidative processes, either photolytic oxidations or biologic processes. The imazamethabenz acid molecule is negatively charged at the ordinary soil pH values [6] and thus the soil colloids are unable to retain the herbicide, this one passing to water. In waters be under strong reductive conditions, associated to very poor or absence of oxigenation (anaerobic waters), it is possible the adsorption of the herbicide on carbonaceous materials present in the waters, this promoting the reductive processes against the UV-photolytic oxidative degradation way, this last one much more effective in natural well sunlighted and oxygenated waters.

ACKNOWLEDGEMENTS

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