THE USE OF MODERN POLAROGRAPHIC TECHNIQUES IN ELUCIDATION OF REDUCTION MECHANISMS OF 1,3,5-TRIAZINE AND PYRIDINE HERBICIDES ON MERCURY ELECTRODES

José Miguel RODRÍGUEZ MELLADO

Departamento de Química Física y Termodinámica Aplicada, Facultad de Ciencias,
Universidad de Córdoba, E-14071 Córdoba, Spain; e-mail: jmrodriguez@uco.es

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Dedicated to the memory of Professor Jaroslav Heyrovský on the occasion of the 50th anniversary of the Nobel Prize for polarography.

The application of differential pulse polarography to elucidation of the mechanisms of electroreduction of some heterocyclic herbicides is presented, showing that modern polarographic techniques are useful in fields different from electroanalysis. The methodology is briefly exposed and the results of its application to reduction of 1,3,5-triazine and pyridine herbicides are discussed.

Keywords: Differential pulse polarography; Electroreduction; Heterocyclic herbicides; 1,3,5-Triazine herbicides; Electrochemistry.

Since the discovery of polarography by Professor Heyrovský, other electrochemical techniques have been developed such as tast, normal pulse, differential pulse or AC polarography. The use of computers in controlling experiments and in further analysis of the data is the key factor for the rebirth of polarographic techniques in the 90's. Out of such techniques, differential pulse polarography (DPP) was developed using dropping mercury electrodes, heavily decreasing the contribution of charging currents in the measured current and, consequently, becoming a widely used electroanalytical technique[1]. The potential–time program consists of a base potential applied during most of the drop lifetime the potential being changed from drop to drop in small increments. Near to the end of the drop life, a 10–100 mV pulse of constant amplitude is applied, measured from the base potential. The current is measured twice: just prior to the application of the pulse and after a time τ (pulse duration), just before the dislodging of the drop. The output of this technique is a graph of the difference between

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these currents, I, vs the base potential. The selectivity and sensitivity of the technique can be increased by controlling both the pulse amplitude and the pulse duration. The differential pulse voltammetry is also a widely used method for routine metal ion analysis.

Study of the I–E relationships allows the use of this technique to elucidate electrode processes, in addition to its use in electroanalysis. Though the equations obtained by rigorous theoretical treatment are difficult to handle to obtain kinetic parameters, approximate equations were developed, allowing kinetic analysis[2,3]. The aim of this paper is to present applications of DPP to elucidation of the mechanisms of the electroreduction of some heterocyclic herbicides.

METHODOLOGY

The methodology used in applications of DPP measurements to the elucidation of the mechanisms of electrode reactions is given in ref.[3] This method is based in the following equation:

$$I = \frac{1}{b}\,\frac{i(i_L - i)}{a i_L + (1-a)i} \qquad (1)$$

where i is the DC polarographic current and I the DP intensity, i_L, is the limiting current in DC polarography, a is a parameter that depends on the reaction order with respect to both the depolarizer and the type of mechanism, and b is so-called logarithmic analysis slope in DC polarography.

All the reductions reported in this paper are first-order processes with respect to the herbicide concentration and, provided that the pulse potential is low enough, Eq. (*1*) can be written as[2,3]:

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

with

$$I_P = i_L/4b \qquad (3)$$

where I_P is the DPP peak current, i.e., the maximum current value obtained at the peak potential, E_P, and L is given as a function of the DC half-wave potential, $E_{1/2}$:

$$L = \exp[-(E - E_{1/2})/b]\ . \qquad (4)$$

Thus, if the process is diffusion controlled or the reaction layer approximation is correct, the experimental DP polarograms obtained can be directly analyzed by using Eq. (*2*). Diagnostic criteria based on the dependence of the b values and variation of E_P with both the reactant concentrations and the pulse duration were obtained.

When the process is diffusion-controlled at the potentials corresponding to the DC limiting current, the i_L values can be used to obtain the number of electrons involved in the electrochemical process by comparison with the reduction of a molecule having a similar diffusion coefficient, and for which the number of electrons involved, n, is known. Since n must be an integer (1, 2, 3, ...), a difference in 10–20% in the diffusion coefficients, which appear as $D^{1/2}$ in the Ilkovic equation, implies a deviation of 4–10% in the i_L values and thus the determination of n is possible. When DPP is used, the comparison must be made by using I_Pb values because this quantity is proportional to i_L as shown in Eq. (*3*).

For handling the equations, the baseline must be subtracted. Two situations were found: (i) the reduction was far enough from the discharge of the supporting electrolyte and (ii) the DP polarogram was distorted due to partial overlaps with such discharge.

In the case (i), the values of the current at potentials lower than the discharge potential can be fitted into a straight line and then extrapolated and subtracted from the overall polarogram. In the case (ii), the contribution of the discharge of the supporting electrolyte can be subtracted assuming that for the supporting electrolyte, I varies exponentially with the potential.

The b parameter must have values close to 12.9, 17.1, 25.7 and 51.4 mV at 298 K (ref.[3]). Experimental results of DPP can be analyzed by measuring half-widths, $w_{1/2}$, E_P and I_P. For first-order processes, the peaks must be symmetrical, and the left and right parts of $w_{1/2}$ must be equal to $3.53b$.

The equality of the right and left parts of $w_{1/2}$ does not ensure that the peak corresponds to a first-order process, since the peak could be symmetrically distorted and, therefore, it is necessary to fit the experimental data using the theoretical equation. If the fit is good and the b values correspond to one of the theoretical values, the process must correspond to one of the mechanisms having this b value. The dependence of E_P on experimental variables will clarify the mechanism: if E_P shifts with pH, the H^+ ion is involved in (or prior to) the rate-determining step (r.d.s.). This variation must be $2.303kb$, k being the reaction order with respect to the H^+ ion. In the same way, b must be concentration-independent.

A variety of cases can be found when overlapped peaks appear depending on both the number of peaks and the degree of overlapping. If the curve shows two overlapped peaks, a good approximation for the *b* values can be obtained by the baseline subtraction from the left part of $w_{1/2}$ for the peak appearing first, and from the right part of $w_{1/2}$ for the second peak. These values are useful in fitting the overall DP polarogram. Moreover, such *b* values, together with variations of the fitted E_P, I_P and *b* with the experimental variables, allow the establishment of the most probable mechanisms for the processes.

In other cases, the peak overlapping prevents obtaining individual peaks and a distorted polarogram results. The following questions must be answered: (i) What is the type of peaks involved? (ii) How many peaks are there? (iii) What are the characteristic parameters of each peak? As for the question (i), if only first-order processes are involved, the peaks must be symmetrical and *b* values must correspond to the process. This is a strong restriction in deconvolution. A small change of experimental conditions must not change the *b* value. In other words, when pH or depolarizer concentration is changed, *b* values of peaks must remain unchanged. As for the question (ii) a minimum number of peaks fitting the polarogram must be used. The change in concentration and/or pH can imply the necessity of using additional peaks to explain the polarogram. Thus, if *b* values obtained under these conditions are retained, then in the starting conditions the experimental and theoretical data must agree using the new peaks in addition to the initial peaks, and this feedback makes credible the deconvolution. The changes in peak potentials and peak currents with pH must be consistent enough to assume that the deconvolution procedure is reasonable.

EXPERIMENTAL

In all cases, Merck analytical grade reagents were used with the exception of 1,3,5-triazine herbicides, which were from Polyscience (HPLC standard quality). The structures of the 1,3,5-triazine herbicides correspond to that shown in Fig. 1. All compounds are crystalline white solids, slightly soluble in water and soluble in organic solvents. Picloram (4-amino-3,5,6-trichloropyridine-2-carboxylic acid) and clopyralid (3,6-dichloropyridine-2-carboxylic acid) are crystalline organics with a chlorine-like odor, slightly soluble in water and soluble in organic solvents.

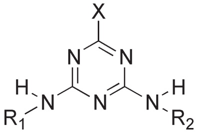

FIG. 1
General structure of 1,3,5-triazine herbicides

The working concentration of substances studied was 2×10^{-4} mol/l, with the exception of the experiments in which the influence of this variable was studied. Solutions of sulfuric acid, for pH < 1, or 0.1 mol/l in both acetic and phosphoric acids, for 2 < pH < 8, were used as supporting electrolytes. Stock solutions of herbicides were stored in the darkness at 277 K to avoid decomposition. Ionic strength was adjusted to 0.4 M with solid NaCl and pH was adjusted with solid NaOH. All potentials were measured against a Metrohm 6.0733.100 $Ag|AgCl|KCl_{sat}$ electrode.

Polarographic measurements were made using a computerized electrochemical system CAEM model SEA-1210. The working electrode was a Metrohm 6-1220.000 capillary. Triply distilled mercury was used. The dropping time was 2 s and the scan rate was 2 mV/s. For DPP, the pulse amplitude was –15 mV and the pulse duration was 50 ms.

RESULTS AND DISCUSSION

1,3,5-Triazine Herbicides

The polarographic behavior of chlorinated 1,3,5-triazine herbicides (X = Cl) atrazine, simazine and propazine was found very similar[4–6]. Above pH 0, a single distorted peak was detected. This peak decreased in intensity and disappeared at pH > 4.

The DP polarograms were deconvoluted into four peaks as shown in Fig. 2 for propazine. Peaks 2 and 3 showed much greater intensities than peaks 1 and 4. The peak current of the peak 2 was of around 2:3 of the peak current of peak 3. The 2.303*b* values of the peaks obtained by curve fitting were

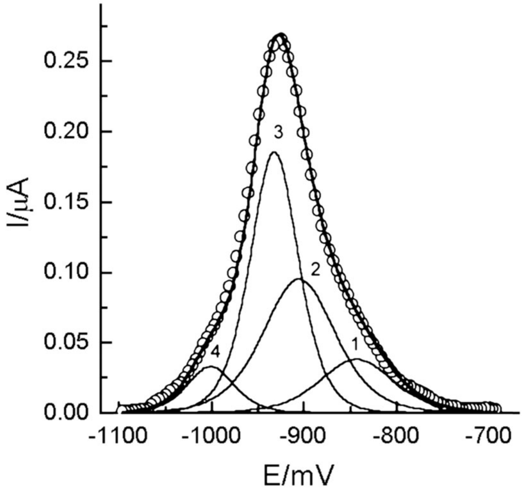

FIG. 2
Deconvolution of the polarogram for 2×10^{-4} M propazine at pH 1.2

60 mV for peaks 1 and 2, and 40 mV for peaks 3 and 4. The areas of peaks 2 and 3 were roughly proportional to the concentration of the herbicides, while the areas of peaks 1 and 4 were independent of this parameter. This indicated that peaks 2 and 3 correspond to the electrochemical reduction process of herbicides, and peaks 1 and 4 correspond to adsorption processes. Peaks 2 and 3 correspond to two-electron reduction processes[5]. Such peaks were attributed[5] to the reductive dechlorination of the herbicide, peak 2, and the subsequent two-electron reduction of the dechlorinated molecule, as in other 1,3,5-triazine reductions[4–6].

The E_P values of propazine are more negative than those corresponding to simazine because the electrochemical reduction is most difficult if the herbicide molecule is larger: propazine has two propyl groups bound to amine nitrogens while simazine has two ethyl groups.

The values of the slopes of the plots E_P–pH, together with the values of the *b* parameter for each peak, supported the idea that the peak 2 corresponds to a CEC (chemical–electrochemical–chemical) process implying the dissociation of the protonated form of the herbicide and subsequent loss of Cl^- ion. So, the reduction mechanism proposed for the chlorinated herbicides is the same[4–6].

The polarographic behavior of (methylsulfanyl)-1,3,5-triazine herbicides ($X = SCH_3$) was investigated[7–9]. A single distorted wave was found that decreased in intensity until it disappeared at pH 4–6. In the pH range studied, the polarograms were deconvoluted into three peaks as shown in Fig. 3 for

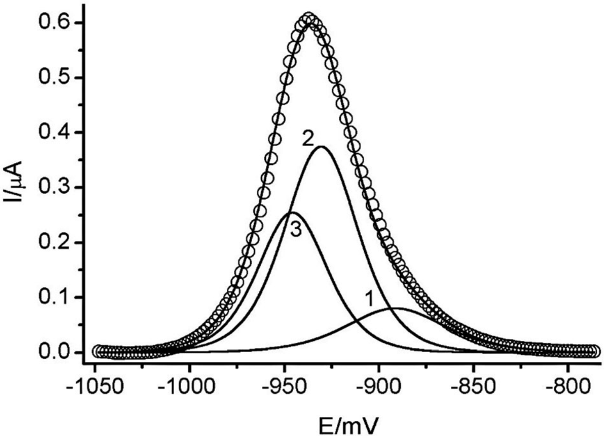

FIG. 3
Deconvolution of the polarogram for 2×10^{-4} M prometryn at pH 2.10

prometryn. Peaks 2 and 3 are the main reduction peaks and showed intensities much greater than peak 1. All the peaks were shifted towards more negative potentials as pH increased, whereas the peak currents varied with pH of the medium from maximum pH-independent values below pH ca. 3.5, to zero above pH 6. Peak 2 showed the highest peak current, the peak current of peak 3 being lower. Finally, the peak current of peak 1 was much lower at high concentrations and similar to that of peak 3 at low concentrations. It was found that the peak area of peak 1 remained virtually unchanged when the herbicide concentration increased. At low concentration values, the peak areas of peaks 2 and 3 were roughly proportional to this variable.

The main peaks corresponded to two-electron irreversible reduction processes, at pH higher than the protonation pK of the triazine ring (around 4). In this pH range, protonation of the triazine ring preceding the reduction process is responsible for a decrease in limiting current. At pH < pK the herbicides suffer a cleavage of the SCH_3 group in two different intermediates related by a chemical reaction, the extent of which depends on the herbicide.

Pyridine Herbicides

In reduction of clopyralid, DP polarograms showed two peaks at pH > 0. Values of I_P and $w_{1/2}$ varied with the solution pH. The DP polarograms were analyzed by assuming the occurrence of at least two peaks. The agreement between the theoretical and experimental values was good, as can be seen in Fig. 4.

The mean 2.303b values obtained were very close (with standard deviations of ca. 2 mV) to 30 and 40 mV for peaks 1 and 2, respectively. The value for peak 3 was 60 ± 2 mV. The peak currents corresponding to peak 1 are greater than the maximum I_P values obtained for peak 2. In addition, the area of peak 2 is lower than the area of peak 1, at pH < 4, though, if these peaks correspond to two-electron processes, the areas must be equal. Moreover, the areas decrease above pH 4 and the overall area also decreases. These two decreases are characteristic of CE (chemical–electrochemical) processes in which the previous chemical step is protonation. From these results, together with those obtained by DC polarography, cyclic voltammetry and controlled-potential electrolysis[10], reaction pathways were proposed[11]. The reduction of the species protonated at the heterocyclic nitrogen corresponds to an EC(EE) scheme (first peak), i.e., a chemical reaction in equilibrium after a reversible electron transfer and followed by the reductions of both species appearing in the equilibrium, as in the case of (methylsulfanyl)-1,3,5-triazines[8].

In the reduction of picloram, DP polarograms showed two peaks in the whole pH range studied. In very acidic media the main peak (peak 1) was observed, accompanied by a shoulder appearing at more negative potentials, which corresponds to a second peak (peak 2) overlapped with peak 1. As pH increased, both peaks shifted to more negative potentials and, at the same time, the overlap of the peaks increased; so, at pH 1.5–2 the polarograms showed one distorted peak in this potential range. A third peak (peak 3) appeared at more negative potentials above pH 3.5–4. Deconvolution of the peaks can be observed in Fig. 5.

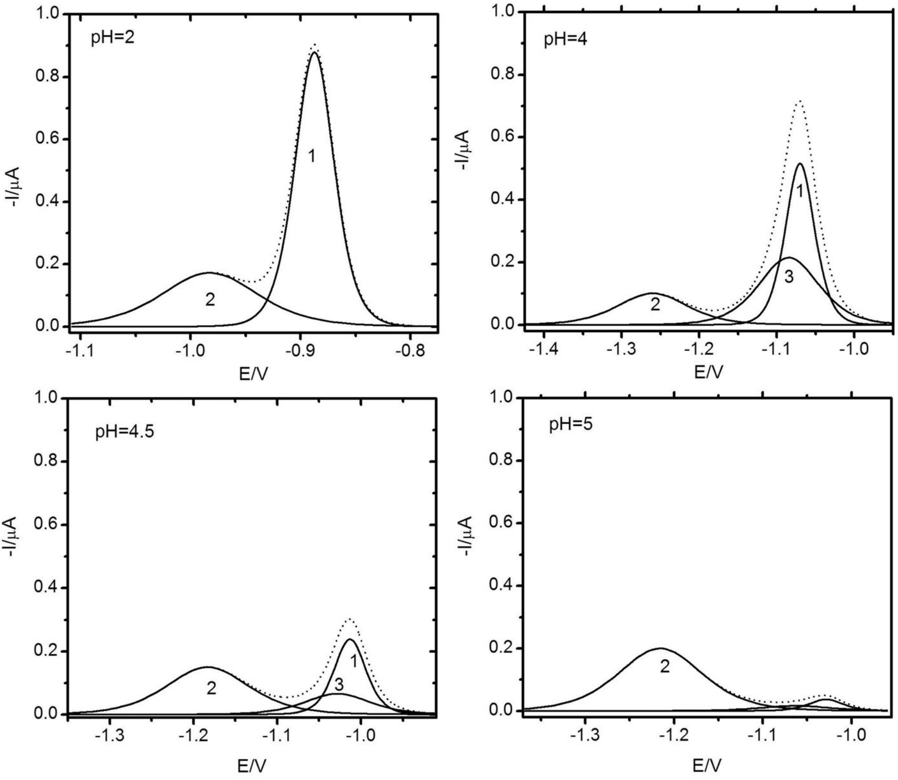

FIG. 4
Deconvolution of DP polarograms of 2 × 10^{-4} M clopyralid. The dotted line represents the whole polarogram

The mean 2.303*b* values obtained for peaks 1 and 2 at pH < 3.5 were very close (with standard deviations of ca. 0.2) to 30 mV. At higher pH, these values changed for peak 1 to 38 mV. For peak 3, the value obtained was near 60 mV. These values are in agreement with the slopes of the logarithmic analyses of the DC polarograms. The area of peak 2 is lower than the area of peak 1, though, if these peaks correspond to two-electron processes, the areas must be equal. In addition, the areas decrease above pH 4 and the peak 3 area also in the pH range 5–7. These two diminutions are characteristic of CE processes in which the previous chemical step is protonation and can be attributed to the dissociation of the COOH and the protonated pyridine nitrogen.

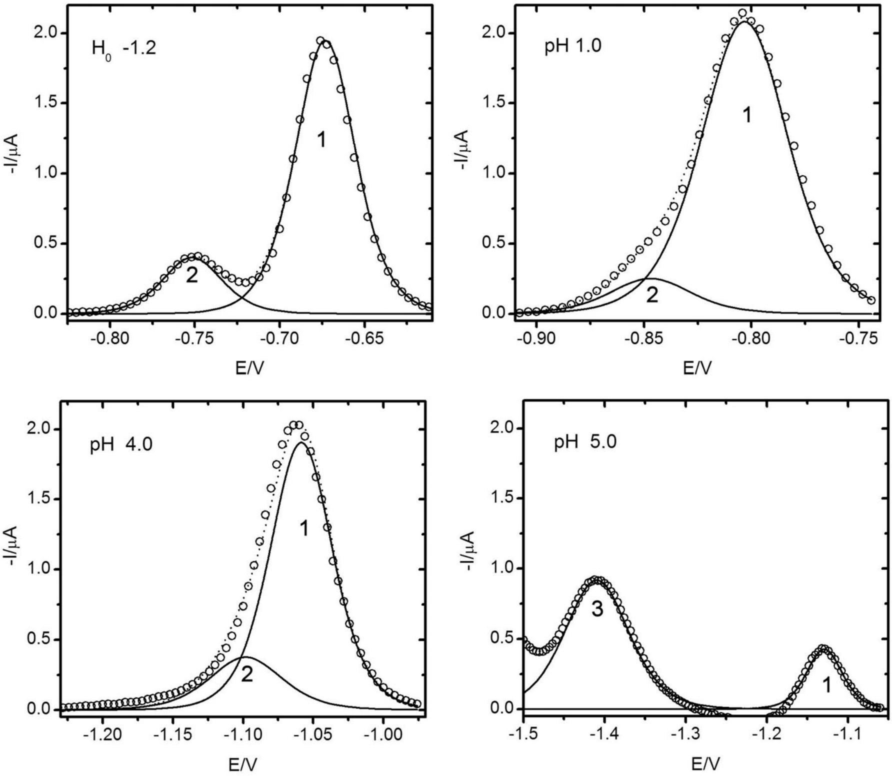

FIG. 5
Deconvolution of DP polarograms of 2 × 10^{-4} M picloram. The dotted line represents the whole polarogram (black line in the figure corresponding to pH 5)

The overall reduction process involves the uptake of four electrons. Kinetic parameters such as the Tafel slopes and electrochemical reaction orders have been determined at the potentials corresponding to the foot of the waves. From these results, together with those obtained by cyclic voltammetry and considering the products obtained after total reduction of picloram on a mercury pool electrode[10], reaction pathways were proposed[12–14]. The reduction of the species protonated at the heterocyclic nitrogen corresponds to an EC(EE) scheme. The acid components of the buffer are involved in the r.d.s., as occurred in the reduction of other pyridine derivatives. At pH > 2 recombination of the carboxylate anion with H^+ ion precedes the reduction process. Peak **3** must correspond to the reduction of the protonated picloram carboxylate.

CONCLUSION

In this paper it is shown that differential pulse polarography is a powerful tool in the elucidation of the electrode mechanisms of organic compounds, specifically in the case of electroreduction of some heterocyclic herbicides. This confirms the actuality of modern polarographic techniques in fields different from electroanalysis.

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