

Electrochemical Reduction and Differential Pulse Polarographic Determination of Butralin and Isopropalin in Environmental Samples at a Mercury Electrode

Mallipattu Sreedhar and Srinivasulu Jayarama Reddy*

Electrochemical Research Laboratories, Department of Chemistry, Sri Venkateswara University, Tirupati-517 502, India

(Received November 29, 2001)

The electrochemical reduction behavior of two dinitroaniline herbicides, Butralin (BN) and Isopropalin (IN), at a mercury electrode is described based on different voltammetric techniques in various buffer solutions at different pH values. The nature of the electrode process has been examined. A reduction mechanism was proposed. Britton–Robinson (BR) buffer of pH 4.0 was found to be best media for the analysis of the compounds. Both standard addition and calibration methods were used for analysis. The detection limits were found to be 6×10^{-8} M (M = mol dm^{-3}) for BN and for 1.5×10^{-8} M for IN. A differential pulse polarographic method was developed for the determination of the herbicides in grains and soils as well as water samples.

Butralin (Fig. 1) and Isopropalin (Fig. 2) belong to dinitroaniline herbicides, and are used as preplant protection agents for agricultural products, such as soybean, cotton, and rice. These herbicides control the unwanted growth of certain broad-leaf weeds.[1] In soil due to microbial degradation, butralin undergoes ring splitting and evolves carbon dioxide.[2] Several analytical methods, mostly chromatographic techniques, are reported for the determination of dinitroaniline herbicides. These are HPLC,[3] GC with mass selective detection,[4] and GC-MS, LC with fluorescence detection.[5] The polarographic method was successfully applied for the analysis of various pesticides, herbicides, and other chemicals used in agriculture.[6,7] The main advantage of the polarographic method is the possibility to use them often without preliminary separations for the analysis of complex biological and environmental matrices; also, these techniques open new analytical possibilities achieving very low detection limits. The DC polarographic behavior of some dinitroaniline herbicides has been studied.[8] Electrochemical techniques[9–11] have been widely used for the determination of nitro group-containing pesticides. No detailed discussion has been given to explain the polarographic behavior of the title compounds by means of polarographic techniques.

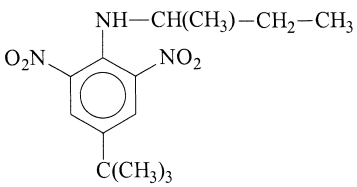


Fig. 1.

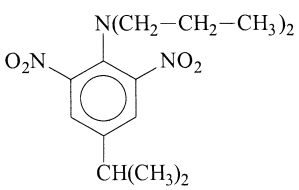


Fig. 2.

This paper deals with the electrochemical reduction behavior of BN and IN with the aid of different voltammetric techniques. Our aim is to develop a differential pulse polarographic method for the quantitative determination of dinitroaniline herbicides, and also to prove that the developed method could also be used for the determination of these herbicides in environmental samples.

Results and Discussion

Preliminary Investigations. Butralin and Isopropalin (1×10^{-5} M) were examined in the following supporting electrolytes and salts: 0.1 M $HClO_4$, 0.1 M H_2SO_4, BR buffer, acetate buffer, borate buffer, and salts such as KCl, KNO_3, $NaClO_4$, and NaCl. The experimental results showed that in all cases the compounds yielded reduction peaks. However, the peaks were clearer, more sensitive, and reproducible in a BR buffer (0.04 M) and KCl (0.1 M).

Effect of the pH. The effect of the pH (varied from 2.0 to 12.0) on the peak potential was examined using differential pulse polarography (DPP) for the two herbicides. In acidic and neutral media (pH $<$ 6) both compounds gave two well-defined peaks (Fig. 3). The peak-height ratios were found to be 2:1. With increasing pH from 6.0, only one peak was observed for BN and IN. The first wave/peak in an acidic medium corresponds to the simultaneous reduction of two nitro groups to hydroxylamine in an eight-electron process, and the second wave/peak attributed to the reduction of hydroxylamine to amine in four electron process. Increasing the pH (pH $>$ 6) corresponds to a decreasing protonation of N-arylhydroxylamine, which in turn results in a decreasing peak current; only

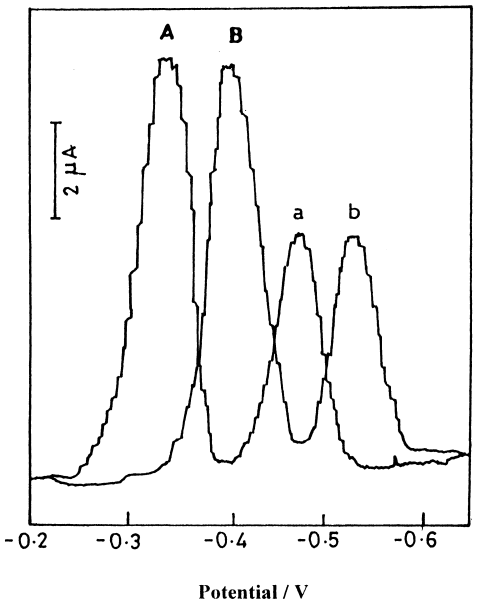


Fig. 3. Differential pulse polarograms of Isopropalin (A: first peak, a: second peak) and Butralin (B: first peak, b: second peak) in pH 4.0, Concentration = 1×10^{-5} M, Drop time = 1.4 s, Pulse amplitude = 40 mV.

four electrons wave/peak was observed corresponding to the reduction of the nitro group to hydroxylamine. As the pH was gradually increased, the peak potential shifted towards more negative values for both compounds, which shows proton participation in the reduction process.

Nature of the Electrode Process. In cyclic voltammetry, BN and IN gave two well- defined peaks in an acidic medium (Fig. 4) and one in a basic medium. No anodic peaks were observed for both compounds. The reduction waves/peaks were displaced to more negative potentials when the scan rate (v) was increased, indicating the irreversible nature of the process. Upon plotting $i_p$vs $v^{1/2}$, a linear relationship was observed as with the diffusion-controlled electrode process, and the slope values were found to be around 0.5 over the entire pH range for both compounds. In differential pulse polarography, we

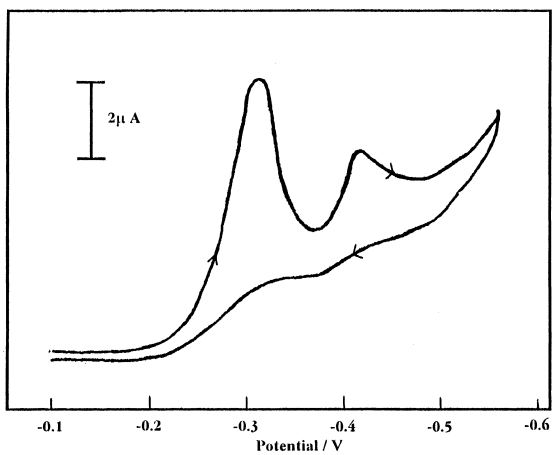


Fig. 4. Cyclic voltammogram of Isopropalin in pH 4.0, Concentration = 1×10^{-5} M, Sweep rate = 50 mV s^{-1}.

observed that the variation of the E_m (E_m = peak potential in DPP) values changed towards more negative potential upon increasing the concentration of the electroactive species; linear plots of i_m (i_m = peak current in DPP) vs $t^{2/3}$ (t = drop time) show that reduction processes of BN and IN were irreversible and diffusion-controlled. When the peak potentials of the two compounds are compared, the reduction of BN is found to occur at more negative potentials than that of isopropalin. The presence of an electron-releasing alkyl group (*tert*-butyl group) on the benzene ring in the *para*-position causes the electron density to increase in BN, which makes the reduction process more difficult than IN, which has an isopropyl group at the same position at the benzene ring. When compared with a previously reported mechanism,[11] there is no formation of a nitroso compound which is responsible for the absence of an anodic peak for both compounds. The nitro group may be directly reduced to hydroxylamine in an eight-electron process. From E_m vs pH plots, the slope values were found to be -70 mV and -68 mV, and the α values were 0.80 and 0.75 for IN and BN, respectively. The number of protons in the rate-determining step were calculated and was found to be around 1.9 and 1.7 for IN and BN using the expression

$$\Delta E_m/\Delta pH = -0.059p/\alpha n_a,$$

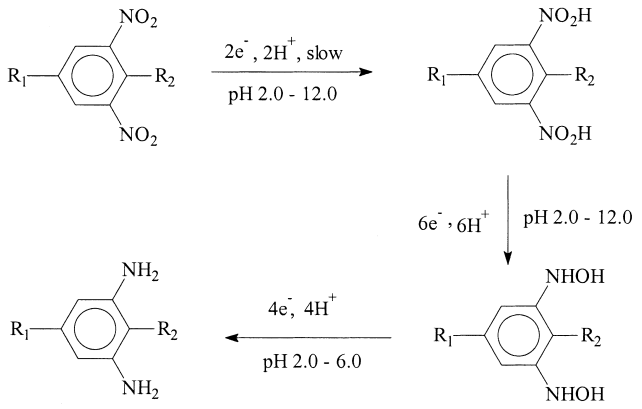
where α is the transfer coefficient, n_a is the number of electrons in the rate-determining step, and p is the number of protons in the rate-determining step.

The number of electrons involved in the reduction processes was calculated from the results obtained by a millicoulometry[12] technique. In an acidic medium, the number of electrons was twelve, and eight in a basic medium for the reduction of two nitro groups. Controlled potential electrolysis was carried out at pH 4.0 and 10.0 for applied potentials of -0.46 V, -0.53 V and -0.69 V, -0.73 V (vs $Ag/AgCl_{(s)}$ Cl^-) for isopropalin and butralin. The reduction products were identified as amine and hydroxylamine through IR spectral data (3200, 3300, 3250, and 3550 cm^{-1}).

Based on the above results of our own investigations as well as from the literature,[8,13] the following mechanism may be proposed for the electrochemical reduction of butralin and isopropalin (Scheme 1).

Recommended Analytical Procedure. Standard stock solutions (1×10^{-3} M) of both compounds were prepared by the dissolving an appropriate amount of electroactive species. To a 10 mL volumetric flask were added an aliquot of standard solution, which was diluted with supporting electrolyte and placed into a polarographic cell. All solutions were stirred and deoxygenated with oxygen-free nitrogen gas through the solution for 5 min prior to analysis. After the polarogramms were recorded, small aliquots of standard solutions were added and polarographic scans were made after each addition under similar conditions. The optimum conditions for the determining these two herbicides at pH 4.0 were found to be a drop time of 1.4 s, a pulse amplitude of 40 mV and applied potentials of -0.32 V and -0.39 V; the relative standard deviation and correlation coefficients were 1.33%, 1.48% and 0.988, 0.992 for IN and BN, respectively.

The above-described procedure was successfully applied for



(R_1 = -C(CH$_3$)$_3$, R_2 = -NH -C(CH$_3$)CH$_2$CH$_3$ for butralin

R_2 = -CH(CH$_3$)$_2$, R_2 = -N(CH$_2$ -CH$_2$ -CH$_2$ -CH$_3$)$_2$ for isopropalin)

Scheme 1.

the determination of these herbicides in environmental samples.

Interference Studies. Under the experimental conditions, substances which are either electroinactive (non-reducible) or reducible at potentials markedly different and more negative than the species under investigation were cut-off. Possible interference of some pesticides, which were frequently applied together with these herbicides, such as atrazine, simizine, and linuron, were tested. Atrazine and simizine gave reduction peaks at -0.95 V and -1.0 V respectively, and linuron did not gave any reduction peaks under the experimental conditions, and consequently did not interfere with the analyte signal. The interference from humic acid was also evaluated. Under the same conditions it did not produce any discernible change in the recovery of these herbicides, even when 60-fold excess was added.

The effect of presence of some inorganic cations such as Zn^{2+}, Pb^{2+}, Cd^{2+}, Cr^{3+}, and Co^{3+} and anions like NO_3^-, SO_4^{2-}, I^-, and Cl^-, which are commonly present in soil and water samples, were tested. The anions, NO_3^- and SO_4^{2-}, did not interfere with the DPP signals of 1×10^{-5} M of BN and IN. In the presence of I^- and Cl^-, the signals of both compounds decreased by about 15%. Inorganic cations, Pb^{2+} and Cd^{2+}, whose reduction potentials are close to the analyte reduction potentials, decreased the peak heights of BN and IN by about 25%. However, the presence of Cr^{3+}, Co^{3+} and Zn^{2+} had no marked effect on the DPP signals of both analytes.

The mutual interference of the herbicides, butralin and isopropalin, was evaluated at a concentration level of 2×10^{-6} M. The interferent molar ratio of IN to BN and BN to IN were 1:0.2 and 1:0.1 with relative errors of 8.0% and 4.0%, respectively.

Quantitative Study. Analysis. For the purpose of analysis, the optimum pH for both (BN and IN) was pH 4.0, where the first peak was sharp and reproducible and was preferred for the analysis. Both standard-addition and calibration methods were employed for quantitative estimations of the compounds. The peak currents were linear over the range 1.2×10^{-5} M (M = mol dm^{-3}) to 7×10^{-8} M, and 1.0×10^{-5} M to 2×10^{-8} M for BN and IN. The detection limits were found to be 6×10^{-8} M and 1.5×10^{-8} M for the respective compounds. The detection limit (DL) was calculated using the criteria 3.S D/m,[14] where SD is the standard deviation, and m is the slope of the calibration plot.

Analysis of Herbicides in Spiked Water Samples. Collected water samples were shaken for a few seconds and filtered through a 0.45 μm filter (Millipore) to remove any particulate material. Aliquot of (50 mL) samples were spiked with BN and IN. After shaking the solution, it was passed through a Sep-Pak plus C_{18} cartridge previously activated with 5 mL of ethanol and 1 mL of deionized water. The analytes were then eluted with 10 mL of dichloromethane and evaporated to dryness in a rotatory vacuum evaporator. The residues of both compounds were dissolved in acetone and transferred into a 50 mL volummetric flask. Differential pulse polarograms of various concentrations of the isopropalin in tap-water samples are shown in Fig. 5. and the recoveries are given in Table 1.

Determination of Herbicides in Grain Samples. 10 mL of the known amounts of analyte solution were added to grain (rice, 20 g) samples and kept in contact for 2–4 h. After this period the samples were extracted with ethyl acetate (3×50 mL) by shaking the flask for 20 min. The organic phase was filtered under suction through Whatmann No.1 filter paper. After evaporation of the solvent, the residues were dissolved in acetone and transferred to a 50 mL volummetric flask. Table 2 gives the recoveries of the herbicides in grain samples.

Determination of BN and IN in Soil Samples. An amount of 20 g of ground, dried soil samples previously spiked with herbicides was extracted with hexane (3×100 mL) by shaking the flask for 10 min. The extracts were then cleaned up twice with 100 mL of acetone and deionized water (1:1 v/v) to remove the interfering organic matter and to avoid the prob-

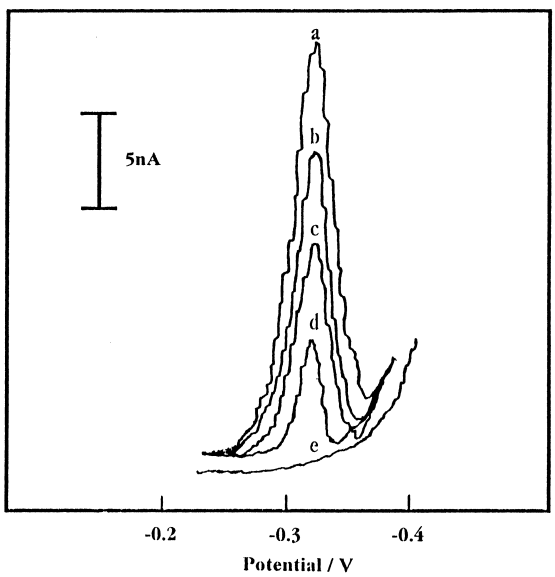


Fig. 5. Differential pulse polarograms of Isopropalin in spiked tap water samples at pH 4.0, Drop time = 1.4 s, Pulse amplitude = 40 mV, a: 1×10^{-5} M, b: 1×10^{-6} M, c: 1×10^{-7} M, d: 1.5×10^{-8} M, e: Blank solution of pH 4.0.

Table 1. Determination of Butralin and Isopropalin in Spiked Water Samples

Compound	Labeled amount mg		Average amount found/mg* ±SD		Average recovery/%	
	Well water	Tap water	Well water	Tap water	Well water	Tap water
Butralin	4.0	5.0	3.93 ± 0.12	4.88 ± 0.22	98.25	97.60
	8.0	10.0	7.82 ± 0.026	9.93 ± 0.052	97.75	99.30
	12.0	15.0	11.91 ± 0.072	14.85 ± 0.061	99.25	99.00
Isopropalin	4.0	5.0	3.87 ± 0.072	4.88 ± 0.061	96.75	97.60
	8.0	10.0	7.93 ± 0.033	9.91 ± 0.033	99.12	99.10
	12.0	15.0	11.80 ± 0.018	14.82 ± 0.066	98.33	98.88

*Each value is an average of four determinations.

Table 2. Recoveries of Butralin and Isopropalin Added to Grains

Compound	Labelled amount/mg	Average amount found/mg* ± SD	Average recovery/%
Butralin	2.0	1.97 ± 0.014	98.50
	4.0	3.89 ± 0.046	97.25
	6.0	5.94 ± 0.033	99.00
Isopropalin	2.0	1.95 ± 0.025	97.50
	4.0	3.97 ± 0.014	99.25
	6.0	5.92 ± 0.029	98.66

*Each value is an average of four determinations.

Table 3. Recoveries of Butralin and Isopropalin Added to Soils

Compound	Labelled amount/mg	Average amount found/mg* ± SD	Average recovery/%
Butralin	3.0	2.92 ± 0.029	97.33
	6.0	5.93 ± 0.051	98.83
	9.0	8.91 ± 0.028	99.00
Isopropalin	3.0	2.97 ± 0.018	99.00
	6.0	5.87 ± 0.068	97.83
	9.0	8.92 ± 0.050	99.11

*Each value is an average of four determinations.

lem of electrode surface saturation. The extracts were evaporated to dryness in an evaporator, and the residue was dissolved in acetone and subjected to polarography. The recoveries are given in Table 3.

Experimental

Reagents. Standard stock solutions of BN and IN (1×10^{-3} M) were prepared in HPLC- grade acetone. BN and IN were obtained from Reidel-de Haen, Germany. A Britton–Robionson (BR) buffer solution was prepared containing 0.04 M acetic acid, orthophosphoric acid, and boric acid. The pH range 2.0 to 12.0 was adjusted with 0.2 M NaOH. All of the solvents and chemicals were of analytical reagent grade. The ionic strength was kept constant with 0.1 M KCl. Triple-distilled water was used for the measurements.

Apparatus. Differential pulse polarographic (DPP) measurements were performed with a Metrohm E-506 Polarecord (Herisau, Switzerland) equipped with a Metrohm-663 VA Stand. Cyclic voltammetric (CV) measurements were carried out using a Metrohm-757 VA Computrace. A dropping mercury electrode (DME) and a hanging mercury drop electrode (HMDE) were used as working electrodes for DPP and CV. The auxiliary electrode was a glassy carbon electrode with a Ag/AgCl (3 M KCl) reference electrode. Using Metrohm-632 pH meter, pH measurements were made. IR spectra were determined by a Perkin-Elmer 1600 spectrometer. Controlled potential electrolysis was performed with a Techno Potentiostat (Model PS-603). All of the measurements were performed at room temperature.

Conclusions

This paper reports on the electrochemical behavior of butralin and isopropalin based on the reduction of the nitro group at DME. The recovery results obtained from the tables show the described method to be simple, reliable and inexpensive, and to represent an alternative method for the determination of these herbicides in environmental samples. The main advantage of the proposed polarographic method over other ones is its sensitivity. Also, because of the possibility of higher sample dilution, less influence of matrix effects and time consuming separation prior to determination is usually not required.

One of the authors M. Sreedhar, is thankful to CSIR, New Delhi for providing financial assistance in the form of a Senior Research Fellowship.

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