Electrochemical oxidation of propanil and related *N*-substituted amides

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Abstract

The electrochemical behaviour of propanil and related *N*-substituted amides (acetanilide and *N*,*N*-diphenylacetamide) was studied by cyclic and square wave voltammetry using a glassy carbon electrode. Propanil has been found to have chemical stability under the established analytical conditions and showed an oxidation peak at +1.27 V versus Ag/AgCl at pH 7.5. *N*,*N*-diphenylacetamide has a higher oxidation potential than the other compounds of +1.49 V versus Ag/AgCl. Acetanilide oxidation occurred at a potential similar to that of propanil, +1.24 V versus Ag/AgCl. These results are in agreement with the substitution pattern of the nitrogen atom of the amide. A degradation product of propanil, 3,4-dichloroaniline (DCA), was also studied, and showed an oxidation peak at +0.66 V versus Ag/AgCl. A simple and specific quantitative electroanalytical method is described for the analysis of propanil in commercial products that contain propanil as the active ingredient, used in the treatment of rice crops in Portugal.

Keywords: Propanil; Anilide herbicides; Square wave voltammetry; *N*-substituted amides

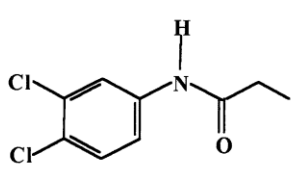
1. Introduction

Anilide herbicides are promising weed control agents for a wide variety of economically important crops, including rice, cotton, potatoes and corn. Among the attractive features of these herbicides are their effectiveness, selectivity and low mammalian toxicity [1–3].

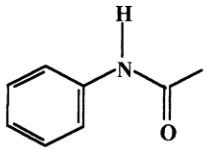
Propanil (3,4-dichloropropioanilide) (Scheme 1) is a selective contact anilide herbicide, recommended for post-emergence use in rice. It is commonly used for the control of broad-leaved and grass weeds [3], and is the only active substance in the phytopharmaceutical products commercialised in Portugal [4].

The degradation of this herbicide has been usually attributed to chemical or enzymatic hydrolysis, microbial breakdown or photolysis. Biodegradation studies revealed that 3,4-dichloroaniline (DCA) (Scheme 1) is one of the principal metabolites of propanil [1,2,5,6]. Propanil is described in the literature [2] to be hydrolysed in strongly acidic and alkaline media to DCA and propionic acid and to be stable over the normal pH range (4 < pH < 9

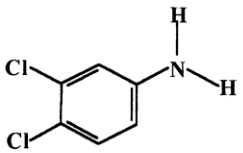
Scheme 1. Structures of propanil, DCA, acetanilide and *N*,*N*-diphenylacetamide.



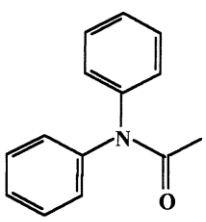
Propanil



Acetanilide



3,4-dichloroaniline (DCA)



***N*,*N*-diphenylacetamide**

at 22°C). It is rapidly degraded in water by sunlight.

One of the most widely used methods for the analytical determination of propanil is gas chromatography with different types of detector [7–10]. Recently the hyphenated technique GC/MS was proposed for the determination of residual pesticides, since it enables specific identification of the different substances and has very good selectivity and sensitivity [10]. However, the equipment is very expensive.

Liquid chromatography has been widely used to quantify propanil [3,11–14]. There is a loss of selectivity and sensitivity in comparison to gas chromatography, but this is compensated by minimisation of thermal decomposition and preservation of the speciation of the compounds in the sample.

Unfortunately, neither of the chromatographic procedures was directly applied to the analysis of concentrated formulations. All of them have measured residue levels in water, soils and crops.

It is essential to obtain information about the behaviour of the pesticides in the environment. Electroanalytical methods, besides the analytical quantification of the pesticide, can provide information about their mechanism of degradation and present other advantages since they are precise, accurate, selective and relatively inexpensive. An electroanalytical method based on the reduction behaviour of propanil has been proposed [15], in which an amperometric sensor was constructed by coating a glassy carbon electrode with a thin layer of a porphyrin catalyst.

In this work, an electrochemical study of the oxidation mechanism of propanil at a glassy carbon electrode is presented. To gain insight into the oxidation mechanism of this herbicide, the electrochemical behaviour of other related *N*-substituted amides (acetanilide and *N*,*N*-diphenylacetamide) (Scheme 1) was studied over a wide pH range. Additionally, an alternative inexpensive, rapid and non-pollutant electroanalytical method that allows the evaluation of propanil in phytopharmaceutical formulations used in rice crops was developed.

2. Experimental

2.1. Reagents and solutions

Propanil was from Riedel de Haen. All reagents were analytical grade and aqueous solutions were prepared using purified water from a Millipore Milli-Q system (conductivity $<0.1\ \mu S\ cm^{-1}$). A stock solution of propanil was prepared in ethanol at a concentration of 1.2×10^{-2} M. Buffer solutions used were in the pH range 1.9–11.9 [16]. The sample stock solution was diluted with buffer electrolyte in order to obtain a concentration within the calibration curve range. Deuteriochloroform was obtained from Cortec.

2.2. Commercial sample preparation

In Portuguese commercial products, propanil is in the form of an emulsion (*Propariz* and *Stam*). A sample stock solution of the emulsion product was prepared by accurately weighing 0.4 g and dissolving it in 50.0 ml of ethanol. The sample stock solution was diluted with 25.0 ml of pH 7.5 Britton Robinson buffer solution of 0.3 M ionic strength [16], in order to obtain a concentration within the calibration curve range.

2.3. Apparatus

All experiments were performed using a 663 VA Metrohm system containing a glassy carbon working electrode (Metrohm 6.1204.000) ($d = 3.0$ mm), a glassy carbon rod counter electrode (Metrohm 6.1247.000) and a Ag/AgCl reference electrode (Metrohm 6.0728.000). This system was attached to a Autolab PSTAT 10 potentiostat/galvanostat running with model GPES version 3 software, from Eco-Chemie, The Netherlands.

The glassy carbon working electrode was polished every day using a polishing kit (Metrohm 6.2802.010) first with α-Al_2O_3 (0.3 μm) and water during 60 s and after with only water during 60 s. After polishing, the electrode surface was thoroughly washed with purified water. The electrode was immersed in supporting electrolyte and cleaned electrochemically by two cycles of applied potential first between -1.1 and $+1.0$ V, resting 30 s at each limit, followed by another between $+0.4$ and $+1.8$ V.

The pH measurements were done with a E 520 pH-meter from Metrohm with a combined glass electrode (Metrohm 6.0202.000).

Melting points were measured using a Köfler microscope. Infrared spectra were recorded on an ATI Mattson Genesis Series FTIR spectrophotometer, using potassium bromide disks (Uvasol, Merck). ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AMX 300 spectrometer operating at 300.13 and 75.47 MHz, respectively. Chemical shifts are expressed as δ (ppm) values relative to tetramethylsilane (TMS) as internal reference and coupling constants (J) are given in hertz. Thin layer chromatography (TLC) was carried out on aluminium sheets precoated with silica gel 60 F254 with layer thickness 0.2 mm (Merck). The following chromatographic systems were used: ethyl ether/ethylacetate (5/5), petroleum ether (40–60°C)/ethyl ether (5/5), chloroform, carbon tetrachloride. The spots were visualised by UV detection (254 nm) and iodine vapour. Solvents were evaporated in a Büchi Rotavapor.

2.4. Synthesis of acetanilide

A pinch of zinc dust was added to a stirred solution of aniline (0.025 mol, 2.3 ml) in acetic anhydride (0.025 mol, 2.4 ml). The suspension obtained was refluxed for 30 min. The hot mixture was filtered and the solution was slowly added to iced water (100 ml). After cooling this mixture in an ice bath, the product was collected by filtration and washed several times with water. Acetanilide was obtained as white crystals. The MP, IR and NMR data were similar to those already described [17–20].

2.5. Synthesis of *N*,*N*-diphenylacetamide

This compound was synthesised according to the procedure described for the synthesis of acetanilide, using *N*,*N*-diphenylamine (0.020 mol, 4.2 g) and acetic anhydride (0.075 mol, 7.2 ml). The reaction was monitored by silica gel TLC, using a 5:5 mixture of light petroleum: ethyl ether as eluent. Complete disappearance of the starting material was observed after 1 h of reaction time. *N*,*N*-diphenylacetamide was obtained as white crystals by the same work-up as that described for acetanilide. The MP and IR are in accordance with the data reported in [20]. ^{1}H NMR ($CDCl_3$, 308.1 K), $\delta = 2.05$ (s, 3H, CH_3), 7.25–7.35 (m, 10H, $2C_6H_5$). ^{13}C NMR ($CDCl_3$, 308.1 K), $\delta = 23.7$ (CH_3), 126.3–128.1, 129.3, 143.1 ($2C_6H_5$), 170.3 (C-amide group).

2.6. Studies on the stability of ethanolic aqueous propanil solutions at different pH values

2.6.1. At room temperature

Two solutions of propanil (0.2 g) and electrolyte (50 ml) in ethanol (20 ml), having different pH values (pH 1.9 and 11.9), were stirred for 36 h at room

temperature. No hydrolysis products were detected by silica gel TLC, either in acidic or in basic solutions. Each ethanolic aqueous solution was then successively extracted with ethyl ether (3×100 ml) and carbon tetrachloride (3×100 ml). The combined organic layers were washed with H_2O and dried (Na_2SO_4). After solvent evaporation, analysis of the crude products by TLC revealed only the presence of propanil.

2.6.2. Under reflux

Two solutions of propanil (0.014 g) and electrolyte (50 ml) in ethanol (20 ml), having different pH values (pH 1.9 and 11.9) were heated under reflux. The reactions were monitored by silica gel TLC, using carbon tetrachloride as eluent. Formation of a new compound was observed. After 5 h the reactions were stopped and the mixture was extracted with carbon tetrachloride (3×50 ml). The combined organic layers were washed with H_2O and dried (Na_2SO_4). The solvent was then evaporated under reduced pressure and the crude products purified by preparative TLC (chromatographic conditions as described above). The compound obtained in both conditions was identified as (DCA). The MP and IR are in accordance with the data reported in the literature [20]. ^{1}H NMR ($CDCl_3$), $\delta = 3.72$ (s broad, 2H, NH_2), 6.49 (dd, 1H, $J = 8.6$ and 2.6 Hz, H-6), 6.74 (d, 1H, $J = 2.6$ Hz, H-2), 7.16 (d, 1 H, $J = 8.6$ Hz, H-5). ^{13}C NMR ($CDCl_3$), $\delta =$ 114.5 (C-6), 116.3 (C-2), 120.9 (C-4), 130.6 (C-5), 132.5 (C-3), 146.0 (C-1).

3. Results and discussion

3.1. Cyclic voltammetry

The electrochemical behaviour of 1 mM propanil in Britton Robinson buffer solution of 0.3 M ionic strength was studied by cyclic voltammetry (Fig. 1). The oxidation reaction is irreversible, diffusion controlled, and suggests that the oxidation occurs at the nitrogen atom of the amide, as will be confirmed later. In acid media, the oxidation products adsorbed very strongly on the electrode surface causing severe poisoning. In order to clarify the oxidation mechanism, propanil-related *N*-substituted amides (acetanilide and *N,N*-diphenylacetamide, Scheme 1) were synthesised and their electrochemical behaviour studied at a glassy carbon electrode.

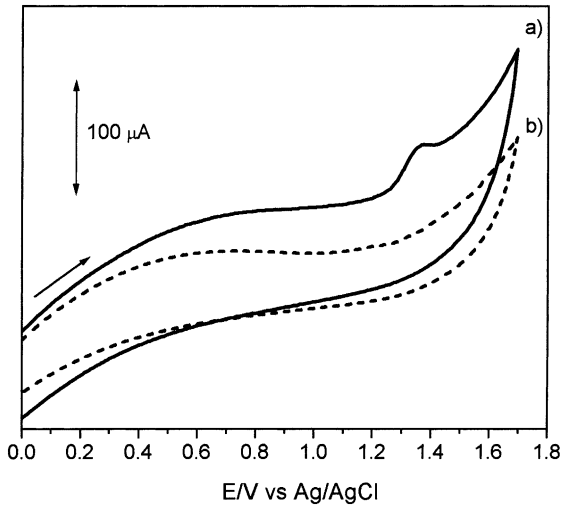


Fig. 1. Cyclic voltammograms: (a) 1 mM propanil in pH 8.0 with 0.3 M Britton Robinson buffer; (b) pH 8.0 with 0.3 M Britton Robinson buffer. Scan rate 100 mV s^{-1}.

3.2. Eletrochemical behaviour with pH of the N-substituted amides

The electrochemical behaviour of propanil, acetanilide and *N,N*-diphenylacetamide, concentration 0.20 mM, was studied using differential pulse voltammetry over a wide pH range from 1.9 to 12.2.

Propanil and acetanilide showed an identical variation of peak potentials with pH, Figs. 2 and 3. A plot of I_p versus pH shows that the oxidation peak current decreases with increasing pH, increasing again for basic pH values. The plot of E_p versus pH shows similar trends for both compounds. For pH < 6 a correlation of 32 mV per pH unit is seen which corresponds to a two electron and one proton reaction. In the interval 6 < pH < 10, the peak potential is pH independent. For pH > 10, the slope is 75 mV per pH unit. Maximum currents were always observed at acid pHs. However, adsorption in acid media was very high, the peak currents diminishing very much in subsequent scans. The best results were obtained in buffer solutions with pH 7.5 and this pH was used in subsequent experiments.

The oxidation of *N,N*-diphenylacetamide is at the disubstituted nitrogen atom, only occurs for pH > 5.2, the peak potential is independent of pH, and the highest currents were obtained at pH 9.7.

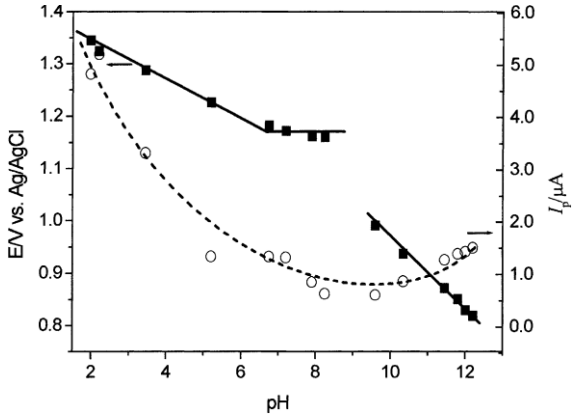


Fig. 2. Plots of (—) E_p and (---) I_p vs. pH from differential pulse voltammograms for 0.20 mM solutions of propanil in 0.1 M ionic strength buffer electrolyte. Scan rate 5 mV s^{-1}.

3.3. Square wave voltammetry of related N-substituted amides

The electrochemical behaviour of propanil, acetanilide and *N,N*-diphenylacetamide, obtained at pH 7.5, for solutions of equal concentration of each amide, 1.7×10^{-3} M, is shown in Fig. 4. Propanil and acetanilide have similar oxidation potentials, +1.27 and +1.24 V, respectively, whereas *N,N*-diphenylacetamide has a higher oxidation potential, +1.49 V. These results are in agreement with the substitution pattern, type and number of substituents

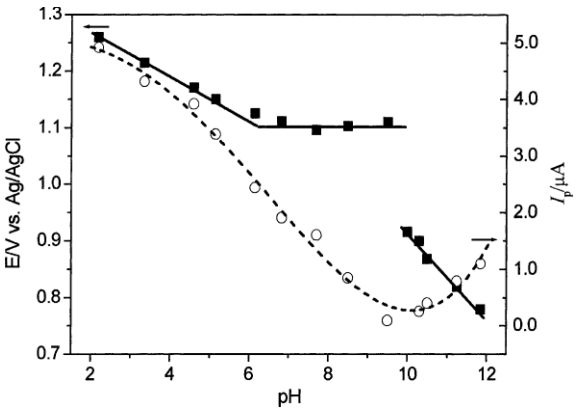


Fig. 3. Pots of (—) E_p and (---) I_p vs. pH from differential pulse voltammograms of 0.20 mM solutions of acetanilide in 0.1 M ionic strength buffer electrolyte. Scan rate 5 mV s^{-1}.

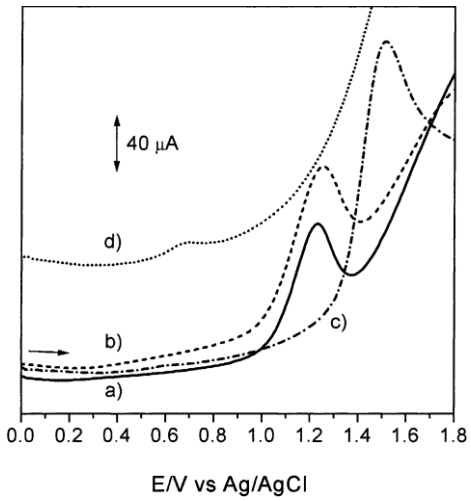


Fig. 4. Square wave voltammograms of 2 mM: (a) acetanilide (—); (b) propanil (---); (c) *N,N*-diphenylacetamide (-·-·-); (d) DCA (···), in pH 7.5 with 0.3 M Britton Robinson buffer. Frequency 50 Hz; potential increment 1 mV; pulse amplitude 50 mV.

of the nitrogen atom of the amide, and confirm that oxidation occurs at the nitrogen.

3.4. Stability of ethanolic aqueous propanil solutions at different pH values

Propanil is described in the literature to be hydrolysed in strongly acidic and alkaline media to DCA (Scheme 1), so it is important to verify its chemical stability under the experimental conditions of the analysis. The study was conducted at room temperature with propanil solutions at pH 1.9 and 11.9, using the same experimental conditions as those in cyclic voltammetry.

Analysis of the reactions by TLC, using different eluents, revealed only propanil, even when the solutions were kept for more than 1 day. All the solutions were also examined electrochemically by differential pulse voltammetry and only the peak corresponding to the oxidation of propanil was observed. In order to confirm these results the reaction was scaled up (see Section 2). No hydrolysis products were found, only propanil was observed.

Hydrolytic degradation of the herbicide was observed only when solutions of propanil were heated under reflux (see Section 2). After purification, the

product obtained was identified as DCA. Thus, under the experimental conditions used for analysis propanil has chemical stability, as chemical hydrolysis only occurs under drastic conditions.

3.5. Electrochemical behaviour of propanil metabolite DCA

Since biodegradation studies showed that DCA is one of the principal metabolites of propanil [1,5,21,22], and in order to probe its possible interference in analytical determinations of propanil, the oxidation of DCA, obtained from the hydrolytic degradation of propanil, was studied at pH 7.5.

The results in Fig. 4 were obtained using separate solutions of equal concentration, 2 mM of propanil or DCA. The peak current for oxidation of DCA ($I_p \sim 5\ \mu$A) at +0.66 V is more than 10 times smaller than that for propanil oxidation ($I_p \sim 60\ \mu$A) at +1.24 V. This significant difference of 0.58 V between the peak potentials means that there should be no overlapping of the peaks.

To confirm this, differential pulse experiments were carried out in a solution containing a mixture of 2 mM propanil and DCA, and no signal could be distinguished at +0.66 V corresponding to DCA oxidation because the peak for propanil was so much larger. Consequently, if DCA metabolite is present in solution it will cause no interference in the electrochemical determination of propanil.

3.6. Determination of propanil in commercial products

Square wave voltammetry was used for the electroanalytical determination of propanil in two commercial compounds, *Propariz* and *Stam*, both of which contain propanil as the active ingredient. The sample and calibration standards, between 2.4×10^{-4} and 6.1×10^{-4} M, were prepared according to the description in Section 2. The calibration plot was a straight line ($y = 0.028 \times 10^{-6}$ to 2.9×10^{-6}, $r = 0.998$, $n = 5$) for propanil. Square wave voltammograms obtained for standards and the commercial sample *Stam* are in Fig. 5. The mean (w/w %) and standard deviation obtained for seven determinations using the electrochemical method for the two commercial samples were 31.7 ± 1.8 (*Stam*) and 29.0 ± 1.7 (*Propariz*).

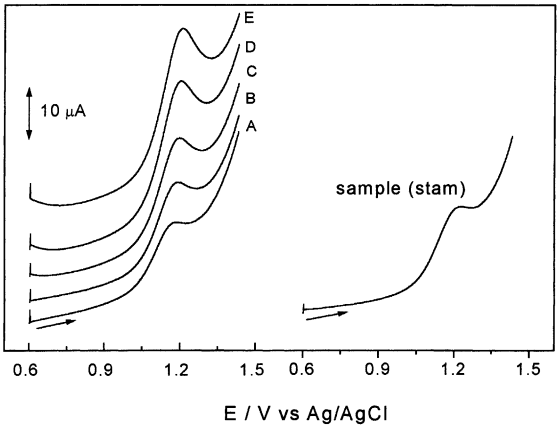


Fig. 5. Square wave voltammograms of propanil in a solution at pH 7.5 with 0.3 M Britton Robinson buffer. Successive additions of standard solutions for constructing the calibration plot ((A) 2.4×10^{-4}; (B) 3.4×10^{-4}; (C) 4.3×10^{-4}; (D) 5.2×10^{-4}; (E) 6.1×10^{-4} M) and a commercial sample solution (*Stam*). Frequency: 50 Hz; scan increment: 1 mV; pulse amplitude: 50 mV.

The recovery data for these seven determinations was 102.2 ± 3.2% for *Stam* and 98.8 ± 4.2% for *Propariz*. Thus, the electroanalytical method is very good for the determination of propanil in commercial products.

4. Conclusions

The electrochemical oxidation mechanism of propanil and two related *N*-substituted amides, acetanilide and *N,N*-diphenylacetamide, was studied. An electroanalytical method was developed for the rapid evaluation of propanil in phytopharmaceutical compounds used in rice crops. The mechanism of oxidation of propanil, which occurs at the nitrogen of the amide, is irreversible and was studied over a wide pH range, showing strong adsorption in acid solutions.

The herbicide formulation is a mixture of propanil (major constituent), additives and wetting agents. Only the major constituent is electroactive and interference effects from the matrix were not observed within the working potential range of the glassy carbon electrode. No interference was observed from DCA, a principal degradation product of propanil, and since the oxidation peaks are very far apart DCA and propanil can be determined in the same sample. Thus, the electroanalytical method can be used for the determination

of propanil in pesticides and as a stability assay for checking propanil (bio)degradation.

Acknowledgements

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