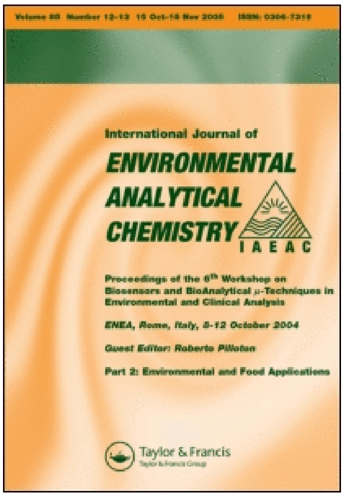

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ELECTROCHEMICAL ELIMINATION OF THE PESTICIDE METHYLPARATHION IN AN AQUEOUS MEDIUM

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One of the most important transformation reactions of methylparathion, an organophosphorus pesticide, was studied. The redox transformation of methylparathion was carried out using different electrochemical methods in an aqueous medium. The study was based on direct current (DCP) and differential pulse (DPP) polarography, cyclic voltammetry (CV) and coulometry. The results show that the pesticide produces a single step or two steps depending on the pH and the electrode. The average value for the limit of detection (3 s) was $(2.05 \pm 0.41) \times 10^{-8}$mol dm^{-3} ($5.4 \pm 1.1$ µg l^{-1}) for DPP. The electrochemical behavior of methylparathion and the nature of the electrolysis products was interpreted according to the electrochemical and spectroscopic data. The experimental data were employed to predict the fate of the pesticide in water samples.

Keywords: Methylparathion; electrochemical elimination; transformation reactions; organophosphorus pesticides; ; polarography

INTRODUCTION

Methylparathion *(Dimethyl-O-(4-nitrophenyl) phosphorothioic acid)* is a common pesticide in use around the world today[1-6]. Between the most important transformation reactions of methylparathion and other organophosphorus pesticides in the environment are chemical hydrolysis, photolysis and redox reactions[7]. An exhaustive bibliographical overhaul of the transformation reactions and methods of detection of this organophosphorus compound reveals two dis-

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tinct aspects: the first works (done in the fifties and sixties)[8-13] were directed to the implementation of analytical methodology for the technical product of the pesticide, and therefore it was not required that methods of analysis be highly sensitive. Hydroalcoholic media or organic solvent water mixtures were used, without attention paid to the effects of the chemical environment on the properties of the compound. On the other hand, more recent investigations during the eighties and nineties[2, 4–5, 14–17] using computerized equipment and highly sensitive chromatographic methods coupled with detectors of high resolution are successfully used in the detection of traces of several pesticides in samples of complex composition, such as river and sea sediments, river and sea water.

It was inferred from literature data that the less studied is the redox reaction. There is lack of some data in the electrochemical behavior of methylparathion in the aqueous medium. The contribution of this work was to evaluate these data and to complement the information available about this topic.

EXPERIMENTAL

Apparatus

The apparatus consisted of a Metrohm 693 VA Processor with a 694 VA stand. A static mercury drop electrode (SMDE), and platinum, gold and glassy carbon disc electrodes were used as working electrodes, a platinum wire as auxiliary electrode and Ag°/AgCl redox system as reference electrode. The cyclic voltammograms were obtained employing a hanging mercury drop electrode (HMDE). The coulometry study was carried out on a Tacussel potentiostat PRG5 model and Tacussel integrator IG5 model, using a mercury pool as cathode and a saturated calomel electrode (SCE) as reference; the platinum mesh counter electrode was placed in a separate compartment.

Reagents

Solutions of methylparathion were prepared by dissolving the solid product (Monsanto) in acetone. A stock Britton-Robinson (BR) buffer solution (pH 1.6) composed of a mixture of boric, orthophosphoric, and glacial acetic acids (all 0.04 mol dm^{-3}) was prepared from analytical grade reagents. From this stock solution, buffer solutions of varying pH were prepared by the addition of a concentrated orthophosphoric acid or sodium hydroxide solution, and the pH measured with a pHmeter.

Procedure

The polarographic study of methylparathion was carried out in aqueous medium at various pH. After bubbling N_2 through the solution for 10 minutes to deaerate it, the corresponding DC, DP or cyclic polarograms were recorded; in the case of DPP the pulse amplitude was –50 mV; for DCP and DPP the scan rate was 6 mV s^{-1} in both techniques. In the case of CV the scan rate ranged from 0.5 to 100 V s^{-1}. The coulometric study was performed in the same medium, and 5×10^{-5}mol dm^{-3} solutions of methylparathion were employed.

RESULTS AND DISCUSSION

Polarographic study

Methylparathion exhibited one or two processes of electrochemical reduction according to the pH of the medium (Figure 1). In very acid medium ($pH < 1.8$) only one very well-defined wave (DCP) or peak (DPP) were seen and six electrons were exchanged in the redox reduction of the nitroaromatic group. For $1.8 < pH < 6$, two reduction processes were observed. The first reduction was a very well-defined wave and the second one was an ill-defined wave; four and two electrons were involved in the redox processes, respectively. In neutral and alkaline medium ($pH > 6$), a reduction process was observed with four electrons involved in the reduction of the pesticide. At $pH > 8$, a hydrolysis reaction of methylparathion occurs[18] which affected the current intensity values, depending on the time and the pH. The number of electrons involved in each reduction reaction was estimated by coulometry, this study is presented in another section of this paper.

An adsorption process, probably of the P=S group of methylparathion and other S-derivative compounds, has been reported.[9] In this work, the peak current intensity (i_p) was very large in comparison with the diffusion current intensity (i_d), and when a second scan was carried out i_p decreased considerably. Nevertheless, the studies of variation of i_d with $h^{1/2}$ (with SMDE) and $\omega^{1/2}$ (with Au, Pt, and C solid electrodes) presented a linear behavior, which indicates a diffusion controlled process[19–20].

Influence of concentration

This study was performed using DPP in the absence of surfactants at pH 3, under stable conditions for methylparathion. Only peak 1 was studied because the sec-

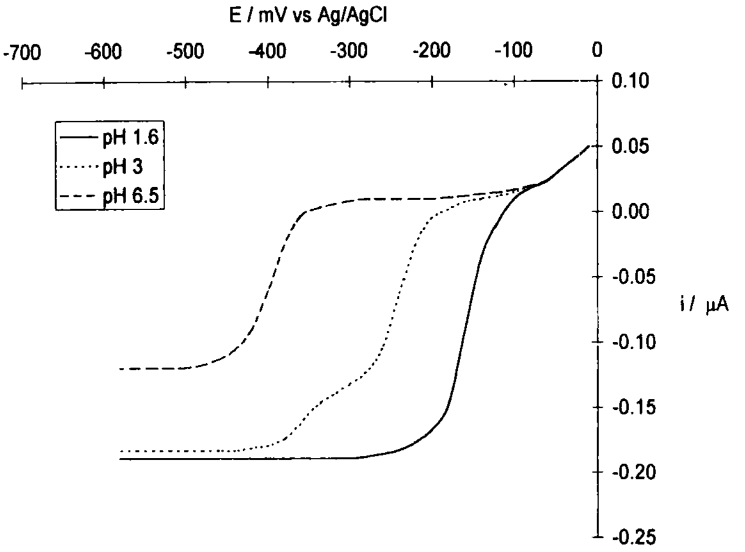


FIGURE 1 DC polarograms of methylparathion in a buffered aqueous medium. 5×10^{-5} mol dm^{-3} methylparathion solutions. Supporting electrolyte: 0.04 mol dm^{-3} BR buffer. Working electrode: SMDE; reference electrode: Ag°/AgCl; auxiliary electrode: Pt. Scan rate: 6 mV s^{-1}

ond one was ill-defined. The relationship found between i_p and the concentration was linear over the entire concentration range studied. The limit of detection values calculated according to the statistical criteria of Long and Winefordner[21–22] and Miller and Miller[23] are shown in Table I.

TABLE I Calibration data (Britton-Robinson buffer, pH 3, T = 25 °C) for methylparathion. S_B, S_m and S_i are the blank, slope and intercept standard deviation, respectively; i is the intercept, m the slope, and t_α the t distribution value ($\alpha = 0.05$)

Polarographic technique	*Slope (m) nA mol dm^{-3}*	*Intercept (i) nA*	*r*	*S_B nA*
DPP	$(2.37 \pm 0.03) \times 10^7$	0.08 ± 0.04	0.9965	0.1749
	10^8 Detection limit (mol dm^{-3})			
	a	*b*	*c*	
	2.21	2.31	2.27	

$a = 3S_B / m$
$b = 3S_B / (m - t\alpha.Sm)$
$c = 3[S_B{}^2 + Si^2 + (i/m)^2.\ Sm^2]^{1/2}/m$

a, b, and c are the limits of detection (in concentration units) calculated acccording to the statistical criteria of the references 21–23.

It was observed that the calculated values of limit of detection employing different statistical criteria were very similar, and the average value for them was $(2.05 \pm 0.41) \times 10^{-8}$ mol dm^{-3} (5.4 ± 1.1 μg l^{-1}). This value was lower than the applied levels used for pesticide treatment in the environment (around 200 μg l^{-1})[24] and it was considered a good limit of detection when compared to studies by Nagniot[9], Reddy and Reddy[25] and Kheifets et al[26–27] that found limits of detection for methylparathion of 500, 10 and 1.1 μg l^{-1}, respectively (studies which also employed electroanalytical methods, though with conditions different from those reported here).

Influence of pH on reduction potentials of methylparathion

A stock BR buffer solution was used in this study, the pH varied for the different conditions by the addition of concentrated ortophosphoric acid or sodium hydroxide solution. DC and DP polarograms were obtained in the pH range of 1 to 13. Methylparathion concentration was constant, 5×10^{-6} mol dm^{-3} in the study. The ratio of buffer to methylparathion concentration was very large and ensured the buffer effect[28]. Four pH predominium zones were observed, they are presented in the E-pH diagram (see Figure 2). In the first three zones the reduction potential of methylparathion depended on the pH, and at pH > 10.8 it was independent of the pH.

When an unbuffered solution was employed (0.1 mol dm^{-3} KNO_3 or 0.1 mol dm^{-3} KCl) in the extreme zones (highly acid or alkaline zones) the strong acid or base acted as a BR buffer, however, in the middle zone the water alone did not act as a buffer system, and an intermediate species was stabilized in a buffered medium but not in an unbuffered one.

This study demonstrated that pH is an important factor that modifies the redox properties of methylparathion and that differences exist if the medium is buffered or not in the described middle pH zone. The qualitative redox behavior of methylparathion apparently is not modified by the presence of different salts employed in the study such as nitrates, chlorides, phosphates, acetates, and borates.

Coulometric study at constant imposed potential

The coulometric study was carried out in a buffered medium in the pH predominium zones mentioned before, and in an unbuffered medium at pH 7. Methylparathion is slightly soluble in water with a maximum of solubility[29] of 2.3×10^{-4} mol dm^{-3} (60 mg l^{-1}). In this work were employed 5×10^{-5} mol

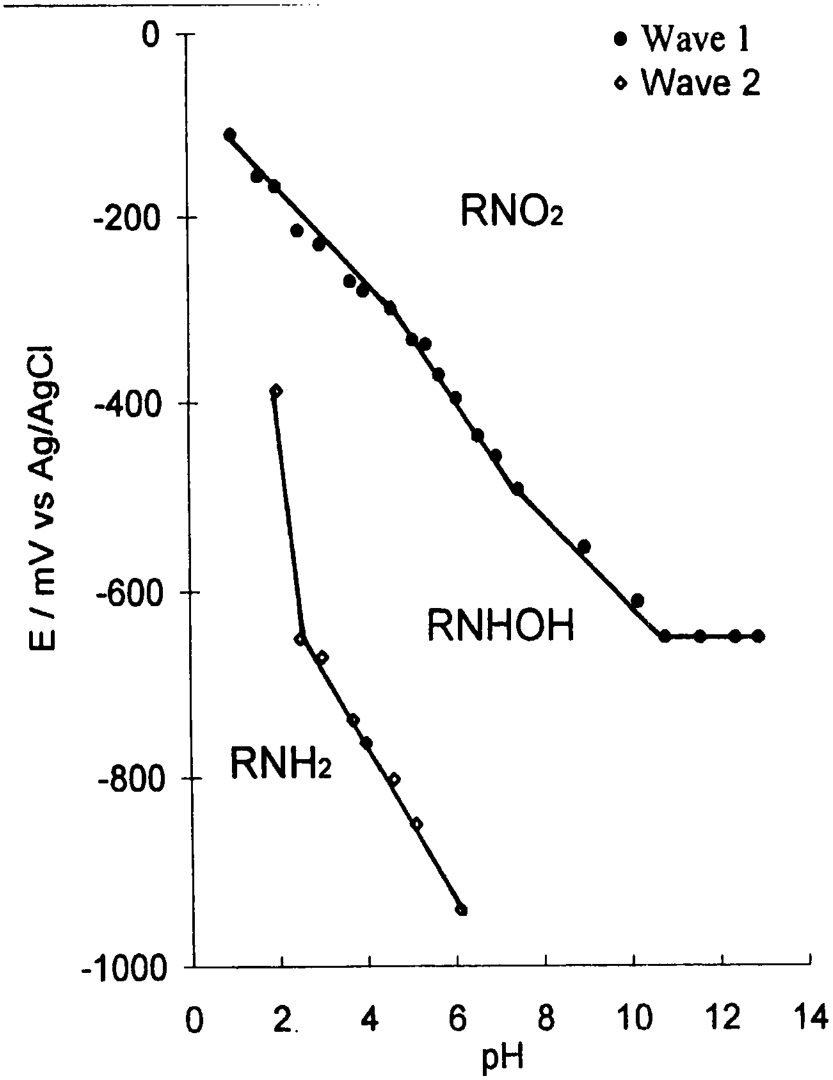


FIGURE 2 Effect of the pH on the reduction potentials of methylparathion in a buffered aqueous medium. Supporting electrolyte: 0.04 mol dm^{-3} BR buffer. Working electrode: SMDE; reference electrode: Ag°/AgCl; auxiliary electrode: Pt. Scan rate: 6 mV s^{-1}

dm^{-3}pesticide solutions. When the electrolysis was conducted at a constant imposed potential of −0.5 V (vs SCE), the decrease in the current intensity only of wave 1 was observed. If the electrolysis was performed at a potential of −1.2 V, the two cathodic waves disappeared (though not simultaneously), and at the end of the coulometry, one anodic wave was seen at pH > 1.8. The reaction products were not stable with time and produced other non-electroactive products in subsequent hours.

In buffered medium, at pH < 1.8, the study of the coulometric curves (μmoles of electrolyzed methylparathion as a function of the number of milicoulombs used up) at an imposed potential of –500 mV (see Figure 3) indicated that six (5.9 ± 0.4) electrons were exchanged in the redox process, corresponding to the electroreduction of the nitro group of methylparathion to the amine derivative in one single step.

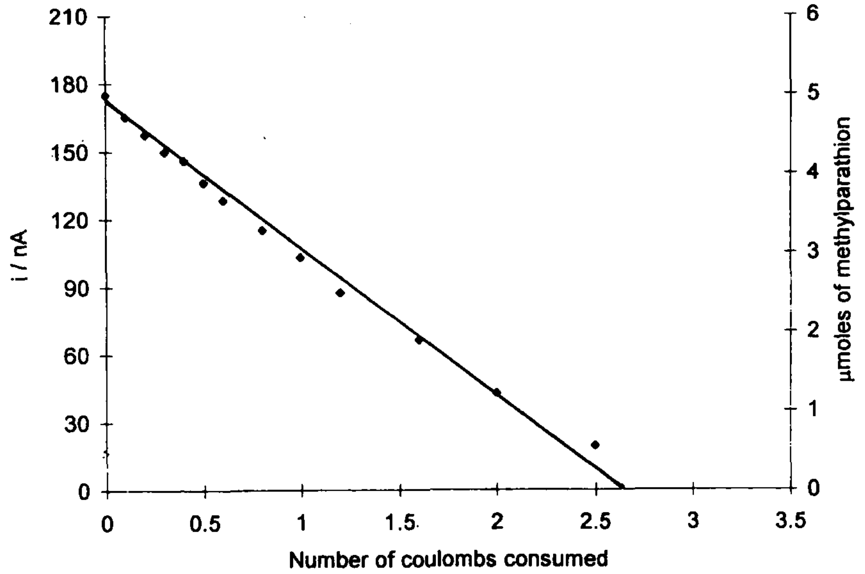


FIGURE 3 Coulometric study. Evolution of the moles of methylparathion as a function of the coulombs consumed in the electrolysis process. pH 1.6, 0.04 mol dm^{-3} BR buffer; E imposed = –500 mV

At 1.8 < pH < 6 two steps were observed and the study of the coulometric curves at imposed potential of-1200 mV (Figure 4) showed that the first step involved four electrons (3.9 ± 0.3) and the second step two electrons (2.0 ± 0.3) corresponding to the electroreduction of the nitro group of methylparathion to the amine derivative in two consecutive steps, with production of the hydroxylamine intermediate. It is possible that the hydroxylamine derivative would be produced at even lower pH, but be very rapidly protoned and impossible to detect by DCP; in less acid medium the protonation step was less rapid and possible to detect. In the 1.8 < pH < 6 region an anodic step was seen and its i_d

increased according to the production of the hydroxylamine derivative in the solution as a result of the electrolysis; therefore, it is reasonable to establish the oxidation of the produced hydroxylamine. This anodic wave was best defined at large pH values. The relationship $i_{d(\text{reduction})} / i_{d(\text{oxidation})}$ decreased at a more alkaline pH, which a major production of hydroxylamine. This situation is observed in the Figures 4 and 5.

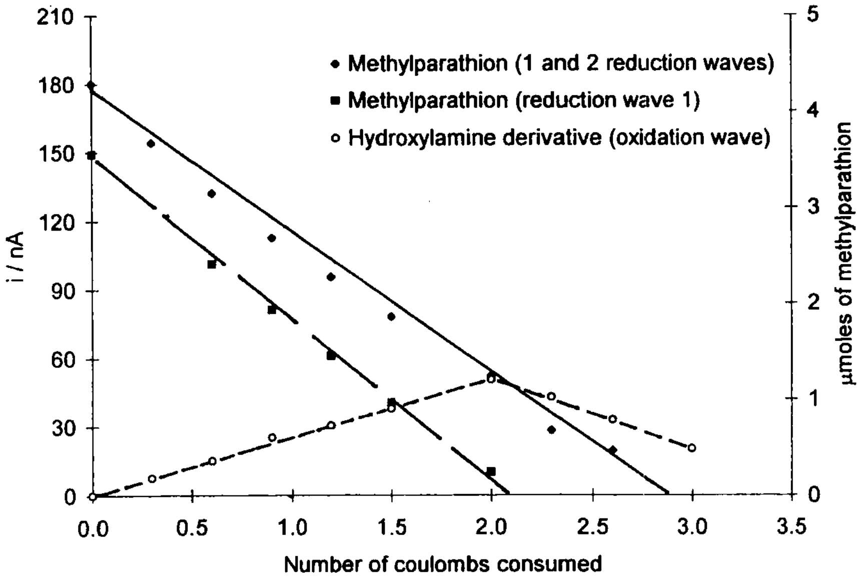


FIGURE 4 Coulometric study. Evolution of the moles of methylparathion as a function of the coulombs consumed in the electrolysis process. pH 4, 0.04 mol dm^{-3} BR buffer; E imposed = −1200 mV

At pH > 6, 3.9×10^5 C mol^{-1} of the methylparathion were consumed (Figure 5), which indicated that four electrons (4.1 + 0.4) were involved in the single reduction step. At this pH range, the protonation step of the hydroxylamine intermediate was slow and it did not produce the amine derivative. The anodic step was seen too, corroborating the presence of the generated hydroxylamine derivative.

The electrochemical behavior of methylparathion was in agreement with the general conduct observed with other nitroaromatic compounds[30,31,32–37] but it was not in concordance with the electrochemical behavior of a similar pesticide, parathion, reported in other studies[8, 38–40], (although the studies were not carried out under the same conditions as those reported here). A parallel electrochemical study was carried out with another nitroaromatic compound,

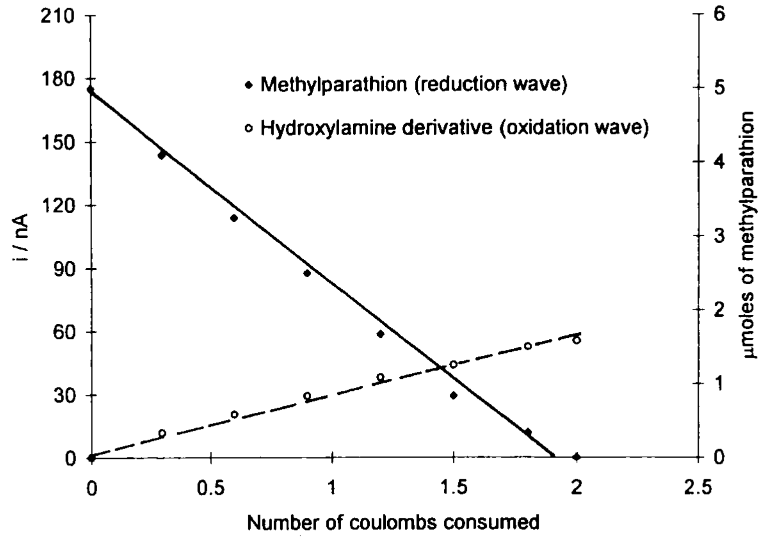


FIGURE 5 Coulometric study. Evolution of the moles of methylparathion as a function of the coulombs consumed in the electrolysis process. pH 8, 0.04 mol dm^{-3} BR buffer; E imposed = −1200 mV

paranitrophenol, employing the same experimental conditions as those used in the methylparathion study and its behavior was different from methylparathion's (these experimental results are not presented in this paper). The dimethylthiophosphate substituent in the pesticide changes the redox properties of the nitroaromatic group.

The coulometric study in unbuffered medium was carried out in 0.1 mol dm^{-3} KNO_3 at pH 7, and the results showed that four (4 ± 0.3) electrons were exchanged in the single step reduction and the final pH value was 11, indicative that the produced compound consumed protons of the unbuffered aqueous medium during its reduction.

Cyclic voltammetry of methylparathion

This study was performed in both buffered and unbuffered mediums. At very acid pH the cyclic voltammogram of the methylparathion with HMDE presented a thin irreversible peak and the produced amine was not electroactive. This behavior conformed to the results described in other sections of this paper. At $1.8 < pH < 6$ (see Figure 6) in addition to the cathodic peak A, an anodic peak (B) was observed in the first scan; after the second scan, an additional cathodic peak (C) at major potential was detected and peak A decreased noticeably, behavior observed only with this cathodic peak in each of the studied pH ranges.

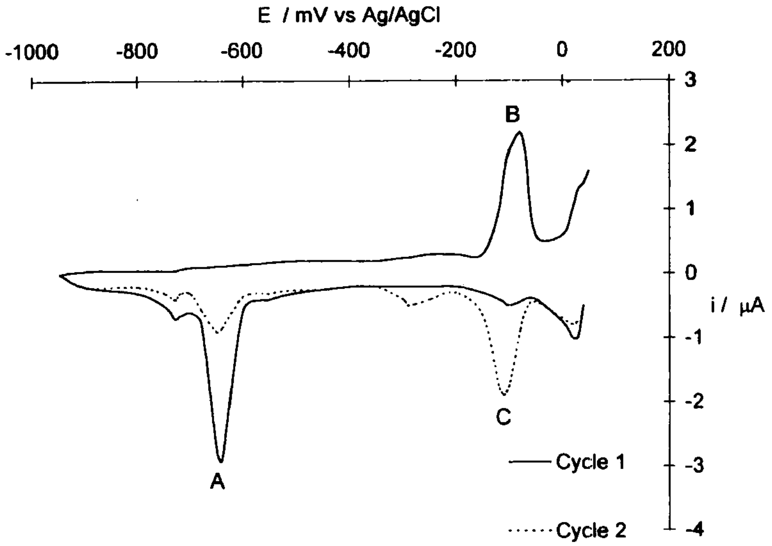


FIGURE 6 Cyclic voltammograms of methylparathion at pH 3.5, in a buffered aqueous medium. Supporting electrolyte: 0.04 mol dm^{-3} BR buffer. Working electrode: HMDE; reference electrode: Ag°/AgCl; auxiliary electrode: Pt. Scan rate: 20 V s^{-1}

The B and C peaks presented similar i_p (i_{pc} / i_{pa} ≈ 0.85) and peak potentials were separated by 30 mV; therefore it is possible that these peaks correspond to the quasireversible system RNHOH/RNO. This behavior was in concordance with the coulometric study where the intermediate hydroxylamine was reduced to the derivative amine and oxidized probably to the nitroso derivative. In the coulometric study it was possible, but not clearly evident, that two electrons were involved in the oxidation of the hydroxylamine derivative, since the maximum i_d of the produced anodic wave was a third of the maximum i_d of the initial reduction wave of methylparathion, which involved four electrons. It is probable that the principal route of the electrolysis did not generate 100 % of the hydroxylamine derivative.

At pH > 6 the cyclic voltammograms of the methylparathion were similar to those of the last zone described, but the peaks were displaced according to the pH.

Spectroscopic analysis of electrolysis products

The products of electrolysis were analyzed by ultraviolet, visible, infrared and mass spectroscopy. The electrolyzed solution adjusted to pH 6.5 was extracted with a (10:1) water-chloroform mixture. The ultraviolet-visible spectrum was obtained from the direct extract. In ultraviolet region all products of electrolysis displayed an absorption band at 245 nm, except p-aminophenol (PAF). The band was associated with the absorption of the aromatic group shifted by the dimethyltiophosphate substituent; it did not present in PAF. A common absorption band was observed at 287 nm, and it was assigned to groups – NH and – OH; this band was more intense in the PAF and the hydroxylamine derivative, since both display joint absorption of groups – NH and -OH. In the amine derivative this absorption is smaller since sustituent -OH in the molecule is not present. The hydroxylamine derivative additionally presented an absorption band at 317 nm that was not observed in the amine derivative. The main products were unstable in normal atmospheric conditions of light, pressure and temperature. In Figures 7 and 8 can be seen the ultraviolet spectra of products obtained by electrolysis at pH 1.6 and 4. It was observed that the band associated with absorption of the amine group diminished noticeably and the absorption band assigned to the aromatic group remained without apparent change; this suggests the transformation of the amine group to other compounds.

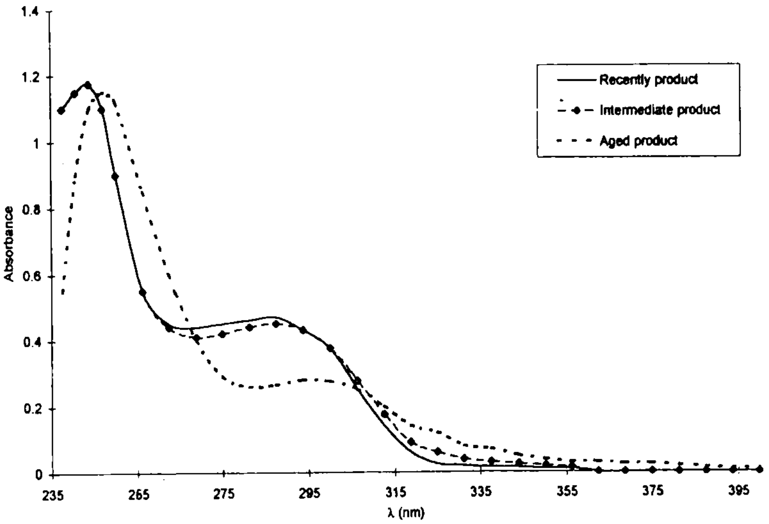


FIGURE 7 Evolution of ultraviolet spectra of Product 1 obtained by electrolysis of methylparathion at pH 1.6 (E imposed = – 600 mV/ECS)

A similar behavior was observed in the IR spectra of electrolysis products. The IR spectra were obtained from the same extract. Spectra of products of electrolysis were compared with those of the methylparathion, the p-aminophenol, and the p-nitrophenol. IR and UV spectra of products obtained at pH 1.6 and 4, and

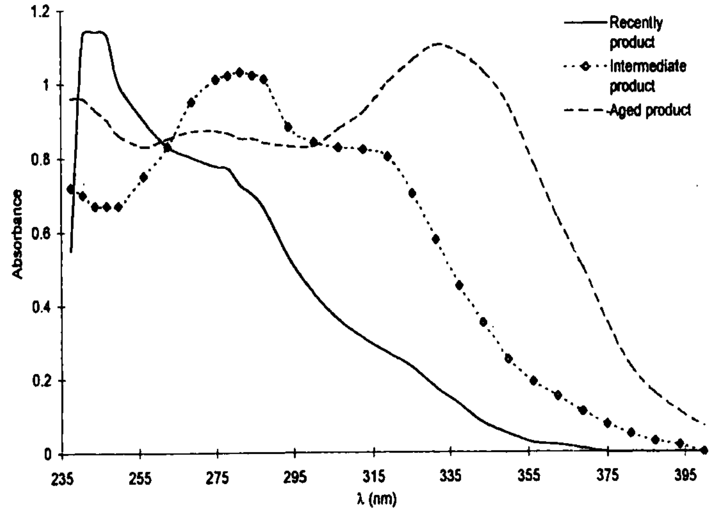


FIGURE 8 Evolution of ultraviolet spectra of product 2 obtained by electrolysis of methylparathion at pH 4 (E imposed = – 600 mV/ECS)

imposed potential = −1.2 V (Product 1), were similar, as much in products just generated as in those of aged products. IR and UV spectra of product obtained at pH 4, and imposed potential = – 0.6 V (Product 2) were different from Product 1. In the IR spectrum of the Product 1 obtained at pH 1.6, was observed the disappearance of the bands associated with the derivative nitro (streching asymmetric C-NO_2 1570–1500 cm^{-1}; streching symmetrical C-NO_2 1370–1300 cm^{-1}), which suggests that this functional group was transformed during electrolysis. On the other hand, the permanence of the band at 1034 cm^{-1}, assigned at P-O-C, leads to the conclusion that the electrolyzed product was an ester.

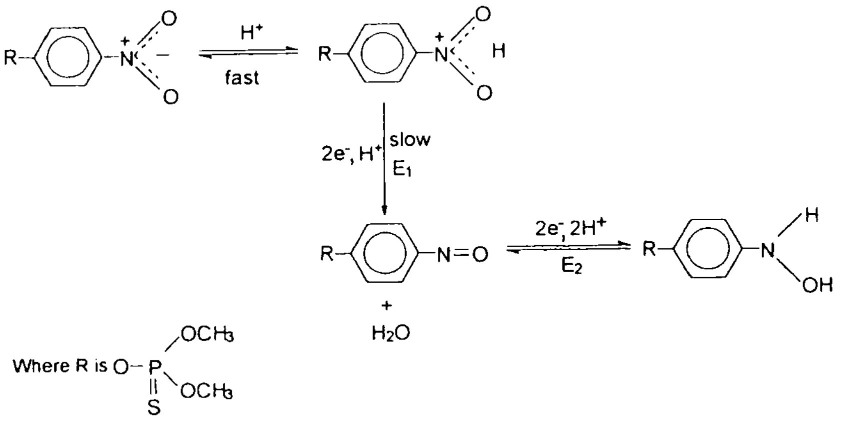
Product 1 was identified as the amine derivative of methylparathion, since the pattern of bands observed in the IR spectrum between 4000 and 3000 cm^{-1} was in concordance with the described one in literature for primary amines[41–42]. IR spectrum of Product 2 displayed a broadband at 3274 cm^{-1} that was associated to the group OH in derivative RNHOH.

In the IR spectrum of the amine derivative appeared a well defined band at 1622 cm^{-1}, that was assigned to the deformation of NH_2 and that exhibits most of primary amines. This band was not observed in the spectrum of Product 2, which confirmed that is not a primary amine.

Experimental results of this part of study were in concordance with the results obtained by coulometry, cyclic voltammetry and polarography.

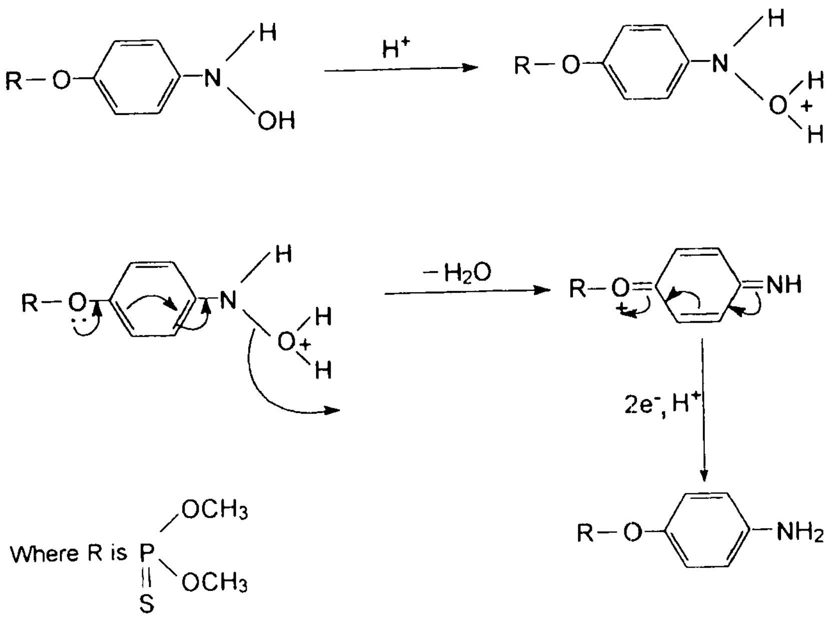
Schemes of reduction

In the following schemes are presented the different steps of the electrochemical reduction of methylparathion in the buffered aqueous medium. Scheme 1 shows the stages in the electrochemical reduction of methylparathion up to appearance of the hydroxylamine derivative. The number of exchanged electrons was verified by coulometry, and the chemical nature of the electrolysis product by spectroscopy. Protonation of the nitro group is fast, the slow process being its reduction to the nitrous derivative, where two electrons are interchanged and an additional proton is taken; next appears the loss of a water molecule and the final reduction of the nitrous derivative to the hydroxylamine derivative. The number of total protons that participate in the global process of reduction depends on pH, as has been mentioned.



SCHEME 1 Electrochemical reduction of methylparathion up to the hydroxylamine derivative

In Scheme 2 are described the stages for the reduction of the hydroxylamine intermediary to the amine derivative. The process begins with the protonation of the hydroxylamine derivative, which requires a rich proton medium; next the elimination of a water molecule occurs to form the quinoide-imin derivative, which quickly reduces to the amine derivative, with exchange of two electrons. The importance of a rich proton medium was made evident by detection of a wave of reduction in the very acid medium, which may be interpreted as the direct step from nitro group to amine derivative. This reaction was less apparent when pH was increased. At pH > 6 this reaction was not observed.



SCHEME 2 Stages for the reduction of the hydroxylamine intermediary up to the amine derivative

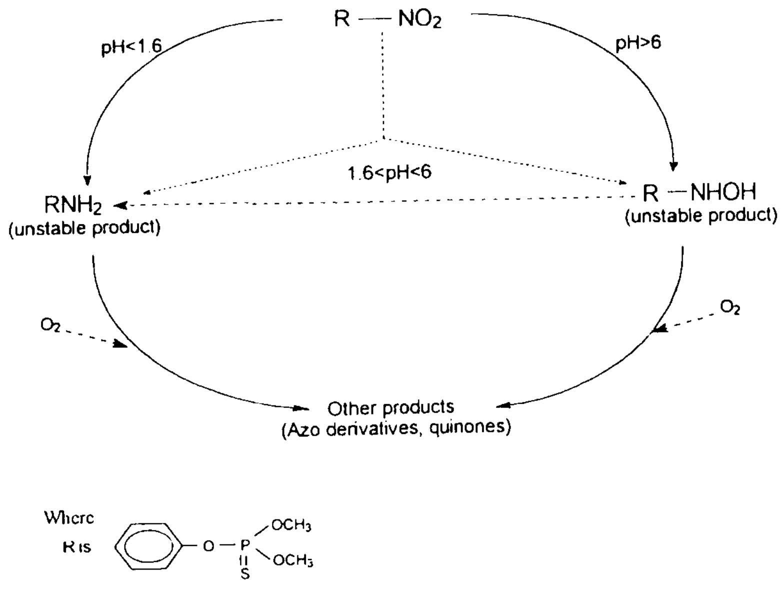
In the E-pH diagram in Figure 2, it can be seen that in almost all zones of pH there were different numbers of protons accompanying the oxidant and the reducer (different slope values were found). The value of any slope depends on the reversibility of the process (values of α), the number of electrons involved in the reduction process, and the number of protons interchanged in the process. At pH > 10.8 was observed the only zone independent of pH, where peak potential or half wave potential remained constant, which implies that the resulting number of protons involved in the electrochemical process was zero. This may have been due to the number of protons exchanged by the oxidant and the reducer being the same, or due to the protons not interchanging in the aqueous medium. The global process at pH >10.8 sets the following reaction:

$$\mathrm{ArN(OH)_2^{2+} + 4e^- \longrightarrow ArNO^{2-} + H_2O}$$

The studied reaction and its applications in waste water that contains the pesticide methylparathion: Prediction of reactions.

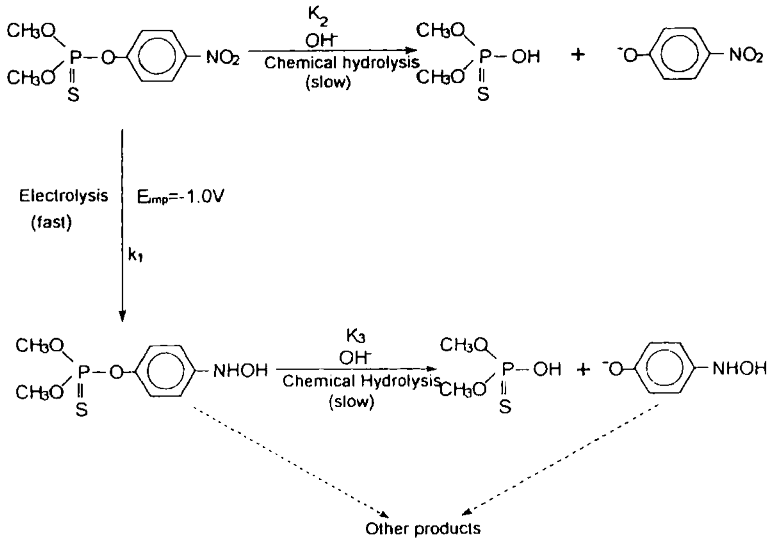
With the information generated in this work it is possible to establish a general perspective of the redox reaction of methylparathion in an aqueous medium and the conditions in which the reaction is favored selectively, as for example in certain pH, in the presence or absence of some chemical agent that would alter the route of the reaction.

In Scheme 3 different routes for the electrochemical reduction from methylparathion are considered. The main products of electrolysis are unstable in normal atmospheric conditions and they are transformed into other compounds. It is observed in this scheme that it is feasible to control the process of electrolysis of methylparathion. Based on pH and the potential imposed, the amine derivative can be produced directly (at pH < 1.6) or only the hydroxylamine derivative produced (at pH > 6), or including the mixture (range of pH between 1.6 and 6).



SCHEME 3 Reduction reactions of methylparathion and subsequent reactions of generated products

Schemes 4 and 5 correspond to predictions that can be established from the experimental results of this work. In Scheme 4, an aqueous solution of methylparathion at pH 8 is presented. In this case its chemical hydrolysis is favored, although according to our results, the reaction occurs slowly. It is feasible, therefore, to carry out the electrolysis to imposed potential ($E_{imp} = -1.0$ V, for example) to produce the hydroxylamine derivative of methylparathion, which in turn is slowly transformed into other products. In both reactions, the final result is a mixture of several products. In a natural water sample of similar characteristics (pH 8 and in the presence of a chemical reducing agent) the nature of possible products from the reactions can be predicted. The relative concentration of these products would be a parameter for evaluating the main route of transformation of the pesticide.



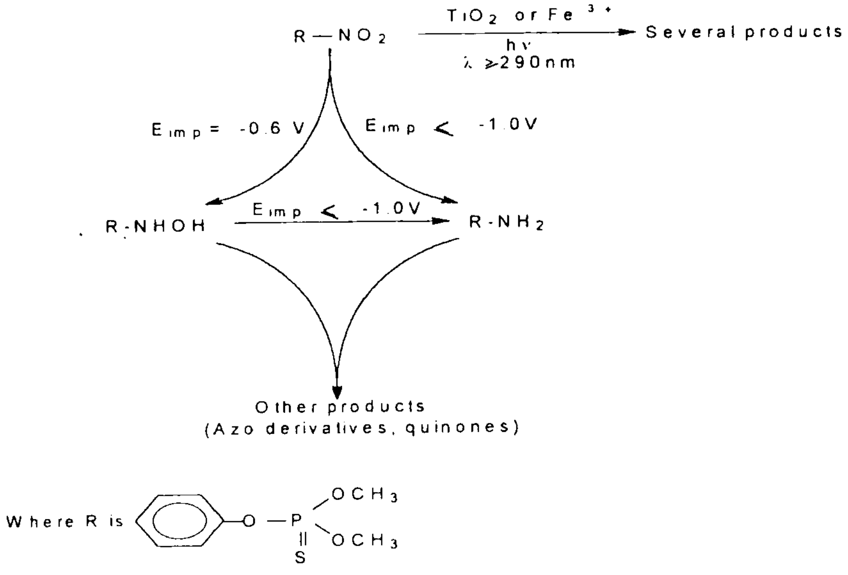
SCHEME 4 Competition between reactions: An aqueous solution of methylparathion at pH 8

In Scheme 5, an aqueous solution of methylparathion at pH 3.5 is employed. In this case, the hydrolysis reaction not being favored, it is possible to utilize the photolysis and electrolysis. Products will be the amine and hydroxylamine derivatives (unstable), which convert to other products. The photolysis produces a product mixture that is dependent upon the presence of photosensitizers.

CONCLUSIONS

The results of this work show the versatile characteristics of electrochemical methods for the study of organophosphorus pesticides, particularly methylparathion.

It is possible to carry out the detection and quantification of this pesticide over a large concentration range. The limit of detection (3 s) is $(2.05 \pm 0.41) \times 10^{-8}$ mol dm^{-3} (5.4 ± 1.1 μg l^{-1}) and sensitivity is $(2.37 \pm 0.03) \times 10^{7}$ nA mol dm^{-3} for DPP. The analysis is economical and fast, the manipulation of the aqueous samples being simple.



SCHEME 5 Competition between reactions: An aqueous solution of methylparathion at pH 3.5

Electrochemical reduction occurs more readily at minor pH, and the final generated compounds are attached to the pH values and are independent of the salts in the medium. Whether the medium is buffered or not is also important in the stabilization of certain compounds. Cyclic voltammetry reveals the presence of intermediate compounds that are not evident with the other electrochemical methods, and complements the information obtained with them.

The electrochemical reduction of methylparathion presents a complex mechanism (not rare in nitroaromatic compounds, as has been demonstrated in multiple works reported in the literature). It is feasible to study the mechanism of electrochemical reduction in a more rigorous manner if one wishes to focus the study on detection and stabilization of intermediary products of short life; this study would have to be made in non-aqueous solvents, a condition in which these intermediaries become stabilized.

On the other hand, methylparathion's elimination is feasible using exhaustive electrolysis in laboratory controlled conditions. It is feasible to predict products generated (or at least which functional groups are present) depending on conditions of pH and reducing chemical agents present in the water. If the intent is to apply the process to clean waste water, it is feasible to eliminate the major bulk of the pesticide and to transform it into innocuous products, using a single method.

The experiments described in this work were made at the laboratory level, but implementation at pilot plant or industrial scale level is feasible. Similarly, its use in field activities it is possible, e.g., the application of technical formulations of the pesticide and destruction of its remainders.

The reaction models allow establishment of methodologies that can be modified according to the specific conditions of the desired reaction. The fundamental study was done with rigorous controls, which would allow use of this information as a starting point for other studies of this pesticide (or pesticides of similar chemical structure) in an aqueous medium, independent of the nature of the studied reaction. When studies have to be made in complex mixtures, the knowledge of the individual behavior of methylparathion under certain conditions of chemical environment represents an advantage, since it is possible to predict its contribution in the product mixture that is detected.

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