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Simultaneous Polarographic Determination of Parathion and Paraoxon. Catalytic Hydrolysis of Parathion by Palladium(II)

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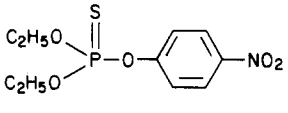
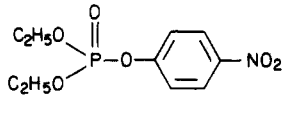
The present work describes an electroanalytical study of the polarographic behavior (DPP) of the pesticides parathion and paraoxon in the presence of Pd(II). This metallic ion shows affinity for the thiophosphate group and catalyzes the hydrolysis of parathion but not paraoxon. A method is proposed for the simultaneous determination of both pesticides based on the fact that parathion can be determined by measuring the *p*-nitrophenol formed after the addition of Pd(II), whereas paraoxon can be measured directly by its reduction peak. In the determination of parathion, acceptable errors were found as long as the parathion/paraoxon ratio is greater than 1/45. In the determination of paraoxon, satisfactory results were obtained for paraoxon/parathion ratios greater than 1/70.

The determination of mixtures of parathion and paraoxon is of great interest from an analytical point of view in part because the control of these pesticides in environmental analyses is important and also because parathion is metabolized in vivo to yield paraoxon and *p*-nitrophenol, among other species (*1*).

parathion



paraoxon



The difficulty inherent to the simultaneous electroanalytical determination of the two pesticides lies in the fact that both of them possess the same electroactive group ($R-NO_2$) and the remaining parts of both molecules are not very different either in size or in polarity. However, *p*-nitrophenol is reduced at more negative potentials, such that the simultaneous determination of parathion or paraoxon with *p*-nitrophenol is possible (*2*, *3*).

The simultaneous electroanalytical determination of parathion and paraoxon has been studied elsewhere (*4*, *5*), although the methods proposed do not seem to have been very satisfactory. Smyth et al. (*5*) have proposed an indirect method based on the different hydrolysis rates in alkaline media; measurements are carried out after 25 min, determining parathion directly and paraoxon by difference. The method is only applicable if the paraoxon/parathion ratio is lower than 3.

In the present work two polarographic procedures (DPP) are proposed for the simultaneous determination of parathion and paraoxon; both of them are based on the different hydrolysis rates exhibited by these pesticides in the presence of Pd(II), a cation which shows a selective affinity for the thiophosphate group (*6*, *7*) and which catalyzes the hydrolysis of parathion but not paraoxon.

Other metallic ions (Cu^{2+} and Hg^{2+}) of known catalytic activity in the hydrolysis of organophosphorus pesticides (*8–10*) were also assayed though the best results were obtained with Pd(II).

EXPERIMENTAL SECTION

Reagents. Solutions of parathion and paraoxon in 50% $MeOH/H_2O$ (v/v) prepared from 99% pure commercial products (Riedel-De-AG, Seelze-Hannover). Solutions of *p*-nitrophenol and of potassium *O,O*-dimethyl thiophosphate were prepared in 50% $MeOH/H_2O$ (v/v). Aqueous solutions of Pd(II) were prepared from $PdCl_2$. Buffer H_3PO_4, HAc, HBO_2, and aqueous solutions of NaOH were also used. All reagents were of analytical grade.

Apparatus. A Metrohm E-506 polarograph, P-Selecta thermostat, and Crison 501 pH meter were used. The electrodes used were Metrohm EA-1019/1 mercury-drop electrode, an auxiliary Metrohm EA-285 platinum electrode, and a KCl saturated calomel electrode.

Procedure. Fifty milliliters of a solution containing parathion and/or paraoxon in 30% $MeOH/H_2O$ medium (v/v), 0.12 M buffer, and variable amounts of NaOH are placed in a cell thermostated at 25 °C. The oxygen is eliminated by bubbling N_2 through the solution for 15 min, and the corresponding polarogram (DPP) is recorded between 0.0 and −2.0 V with a pulse amplitude of −50 mV and a scan rate of 4 mV s^{-1}. Following this, variable amounts of Pd(II) are added, and the concentration of *p*-nitrophenol in the solution is followed polarographically or amperometrically with time. The pH was measured with a glass electrode calibrated with aqueous buffer solutions. The pH value measured is corrected to obtain true values of proton activity in hydroalcoholic medium (pH* = pH − 0.05).

RESULTS AND DISCUSSION

Reaction of Parathion and Paraoxon with Pd(II). In 50% (v/v) $MeOH/H_2O$–0.1 M HAc–0.1 M NaAc medium,

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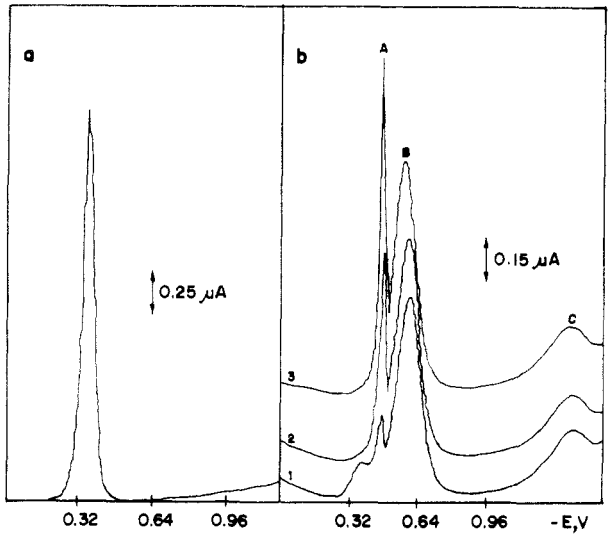

Figure 1. (a) Polarogram of 1.54×10^{-4} M parathion–50% MeOH/H_2O (v/v)–0.1 M HAc–0.1 M NaAc. (b) The previous solution plus 1.98×10^{-4} M Pd(II): (1) 3 min, (2) 30 min, (3) 90 min.

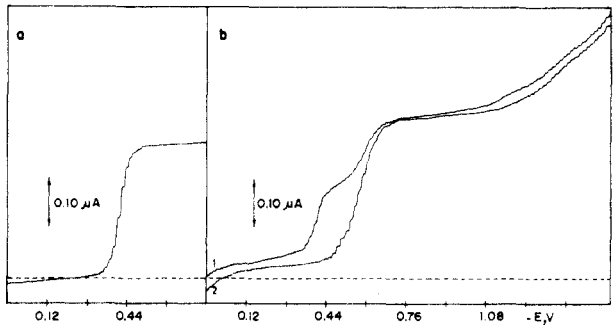

Figure 2. (a) Polarogram of 1.98×10^{-4} M parathion–50% MeOH/H_2O (v/v)–0.1 M HAc–0.1 M NaAc. (b) The previous solutions plus 1.0×10^{-4} M Pd(II): (1) 3 min and (2) 30 min.

parathion shows a well-defined reduction peak (DPP) at −0.376 V (Figure 1a). The addition of Pd(II) induces a progressive decrease in peak height with time, together with the appearance of three new reduction peaks at −0.480, −0.590, and −1.340 V, which are labeled A, B, and C, respectively (Figure 1b). After 15 min, the parathion peak is no longer preceptible, and those obtained at −0.590 and −1.340 V attain a constant value; however, the −0.480 V peak increases progressively with time. In dc polarography (Figure 2a,b) it is seen that peaks A, B, and C are reduction peaks. Upon adding Pd(II) the free Pd(II) wave appears, which decreases with time as the hydrolysis of parathion progresses; however, working in dc waves A and B overlap.

Hydrolysis of parathion results in the formation of *p*-nitrophenol and *O,O*-diethyl thiophosphate (*1*). Peaks B and C have been proved to correspond to the reduction of *p*-nitrophenol to hydroxylamine and amine in this medium by comparison of peak potentials and ratio i_p^B/i_p^C with peaks of authentic *p*-nitrophenol. Peak A corresponds to the reduction of Pd(II) complex with *O,O*-diethyl thiophosphate, as proved by curves obtained for a solution containing Pd(II) and *O,O*-dimethyl thiophosphate (as diethyl ester was not available). These curves show a peak at −0.48 V, with the same morphology as the peak obtained in the presence parathion. The identification was further supported by similar time dependence of the peak in the above mixture and peak A of parathion. The peak at −0.48 V is attributed to the reduction of Pd(II) from a complex with thiophosphate that is slowly formed from Pd(II) (reduced at very positive potential) and the thioester.

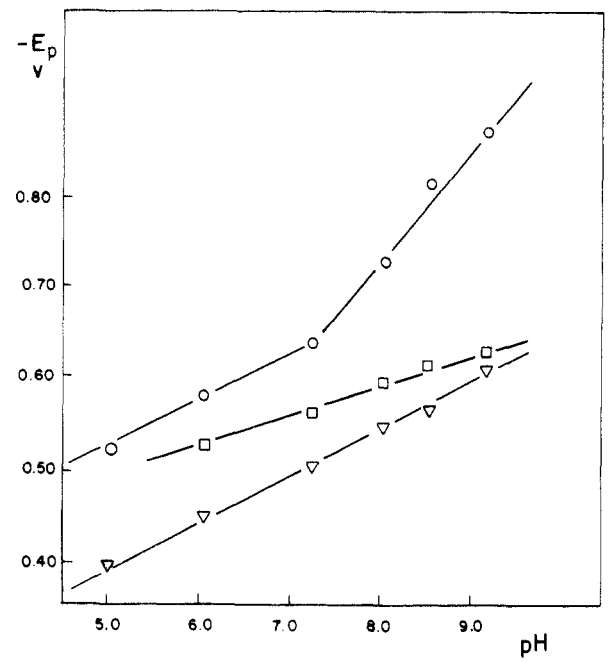

Figure 3. Variation of peak potentials with pH in a solution of 1.03×10^{-4} M parathion, 5.17×10^{-5} M Pd(II), 0.12 M buffer, 30% MeOH/H_2O (v/v), and variable amounts of NaOH: (▽) parathion and paraoxon, (□) Pd–*O,O*-diethyl thiophosphate, (○) *p*-nitrophenol.

The hydrolysis mechanism must be different from that proposed by Mortland and Raman (*11*) for the hydrolysis of the pesticides Dursban, Diazinon, Ronnel, and Zytran in the presence of Cu(II). According to these authors, a coordinated species of Cu(II) and the pesticide is formed; following this, the complex is broken down, hydrolyzing the pesticide and releasing the Cu(II). In our case the Pd(II) forms a complex with parathion, and after the cleavage, the Pd(II) does not remain free because it also forms a complex with *O,O*-diethyl thiophosphate, which is a hydrolysis product.

To be catalytically active, Pd(II) must not be bound in very strong complexes, e.g., with EDTA. In a solution containing 0.1 M HCl or 0.1 M HAc, 0.1 M NaAc, and 0.1 M EDTA no hydrolysis is observed over a period of 2 h. The rate of hydrolysis increases with increasing Pd(II) concentration, but when concentration of Pd(II) is higher than that of parathion, Pd(II) is reduced to metallic Pd by methanol. This precipitate also appears on adding Pd(II) to 50% (v/v) MeOH/H_2O solutions. Such reduction can be prevented by adding EDTA or replacing methanol by acetone, but in either case the rate of hydrolysis of parathion is slower than in aqueous methanolic solution. Optimum conditions for hydrolysis were found in buffer HAc–H_3PO_4–HBO_2, pH* 8–9.5, containing 30% (v/v) methanol. Under such conditions reduction of Pd(II) (present in 1.0×10^{-4} M concentration) did not occur even when concentration of parathion was 1 order of magnitude lower. Moreover, in such solutions the hydrolysis of parathion is sufficiently rapid whereas that of paraoxon does not take place for a period of 72 h.

Optimum conditions for analyses of samples of parathion and its mixtures with paraoxon, based on hydrolysis of the former and measuring the peak of *p*-nitrophenol formed, will depend on separation of individual peaks on DPP polarograms and on the composition of the reaction medium.

Peak potentials of parathion, paraoxon, *p*-nitrophenol, and the complex of *O,O*-diethyl thiophosphate with Pd(II) are shifted with increasing pH to more negative values, but the slopes of the individual E_p–pH plots differ (Figure 3). At lower pH* values the peak of paraoxon is most positive and least well separated from those of *p*-nitrophenol and the Pd–thiophosphate complex. Such conditions (pH* ≃5) are

Table I. Variation of Peak Intensity of the Pd(II)-*O,O*-Diethyl Thiophosphate Complex with the Concentration of Parathion[a]

concn of parathion, 10^{-5} M	L/M	i_p, μA pH* 8.0	i_p, μA pH* 9.25
0.95	0.096	0.026	0.022
1.89	0.19	0.062	0.050
3.78	0.39	0.16	0.14
4.72	0.48	0.17	0.15
7.56	0.77	0.22	0.18
9.45	0.96	0.34	
11.30	1.15	0.28	0.26
14.20	1.45	0.26	0.24
18.90	1.98	0.16	0.21

[a] 9.8×10^{-5} M Pd(II), 30% MeOH/H_2O (v/v), T_a 25 °C, t = 2 s, ΔE = −50 mV (i_p measured after 120 min).

thus best suited if only paraoxon is to be determined, following hydrolysis of parathion. If, on the other hand, only parathion should be determined, pH* ~9 is most suitable, as under these conditions the peak of *p*-nitrophenol is best separated from the other peaks. Simultaneous determination of parathion and paraoxon can be best carried out at pH* ~8 where the three peaks are best separated.

A decrease of concentration of parathion with time does not follow simple first- or second-order kinetics, but shows an induction period. The rate of hydrolysis following the induction period decreases somewhat with increasing pH*. The length of the induction period, on the other hand, increases with increasing pH*. As the reaction rate is independent of addition of an excess of *p*-nitrophenol and as the hydrolysis becomes slower when parathion is added to a solution in which the hydrolysis of parathion in the presence of Pd(II) already occurred, the autocatalytic nature of the process can be excluded and occurrence of the induction period can be attributed to a system of consecutive reactions.

The dependence of current on time at −0.544, 0.592, and −0.728 V (Figure 4) was attributed to concentration changes of parathion, Pd–*O,O*-diethyl thiophosphate complex, and *p*-nitrophenol, respectively. Curves for *p*-nitrophenol and the Pd complex show induction periods indicating a system of consecutive reactions.

One of the schemes that corresponds to concentration changes in Figure 4 is

$$\text{parathion} + \text{Pd(II)} \rightarrow \text{Pd–parathion} \quad (1)$$

$$\text{Pd–parathion} + H_2O \rightarrow p\text{-nitrophenol} + \text{PdA} \quad (2)$$

$$\text{PdA} \rightarrow \text{Pd–}O,O\text{-diethyl thiophosphate} \quad (3)$$

under the assumption that the Pd–parathion complex is reduced with the same number of electrons and at practically the same potential as parathion and that the adduct PdA is not reducible in the studied potential range.

Stoichiometric composition of the Pd–thiophosphate complex cannot be established from electrochemical data as the peak A (Figure 1b) is not diffusion controlled and is probably affected by adsorption (vide supra), Table I.

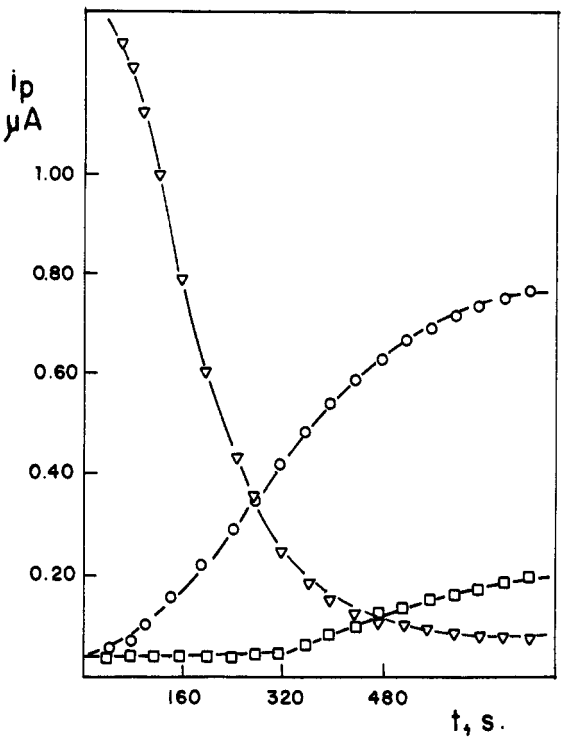

Figure 4. Hydrolysis reaction of parathion with Pd(II) in a solution of 1.04×10^{-4} M parathion, 1.01×10^{-4} M Pd(II), 0.12 M buffer, 30% MeOH/H_2O (v/v), 0.35 M NaOH (pH* 8.0): (▽) parathion, (○) *p*-nitrophenol, (□)Pd–*O,O*-diethyl thiophosphate.

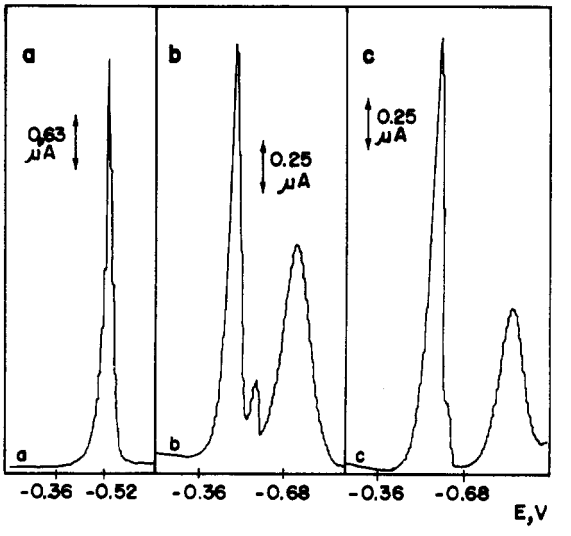

Figure 5. Polarograms of parathion and paraoxon: (a) 1.4×10^{-4} M parathion, 1.16×10^{-4} M paraoxon, pH* 8.0, (b) previous solution plus 1.0×10^{-4} M Pd(II), (c) previous solution at pH* 9.25.

DETERMINATION OF PARATHION AND PARAOXON

The relationship between the peak intensities and the concentration of paraoxon is linear (Table II). For the determination of parathion, the relationship between the con-

Table II. Calibration Analysis[a]

sample	pH*	slope, μA mM^{-1}	intercept, μA	corr coeff	SD residual, μA	10^7LC,[b] M a	b	c
paraoxon	8.0	17.24 ± 0.19	−0.032 ± 0.02	0.999	0.0006	1.03	1.06	28.7
p-nitrophenol	8.0	7.20 ± 0.14	0.016 ± 0.02	0.998	0.0004	1.54	1.65	65.1
p-nitrophenol	9.25	5.91 ± 0.08	−0.002 ± 0.009	0.999	0.0005	2.39	2.50	46.4

[a] Data obtained in DPP; ΔE = −50 mV; t = 2 s. [b] LC, limiting concentration: a, b, and c, see ref 12.

Table III. Determination of Parathion in the Presence of Paraoxon[a]

parathion added, 10^{-5} M	parathion/paraoxon	recovery, % pH* 8	recovery, % pH* 9.25
11.6	122	99.1	97.4
14.5	50	98.6	99.3
9.6	25	102.9	102.1
11.6	12	103.4	100.9
11.6	1	112.0	97.4
0.96	1/12	106.8	106.8
0.426	1/22	37.1	98.8
0.319	1/45	32.9	105.3

[a] 1.04×10^{-4} M Pd(II); for other conditions see Figure 4.

Table IV. Determination of Paraoxon in the Presence of Parathion[a]

paraoxon added, 10^{-5} M	paraoxon/parathion	recovery, %
11.4	108	98.8
14.2	44	98.6
9.5	22	98.5
11.4	12	104.4
11.4	1	98.2
0.95	1/12	105.4
0.379	1/34	104.2[b]
0.284	1/70	89.8[b]

[a] 1.04×10^{-4} M Pd(II). For experimental conditions see Figure 4. [b] Obtained by the standard addition method.

centrations of this pesticide and the peak magnitude of the *p*-nitrophenol formed in the presence of Pd(II) at pH* 8.0 and 9.25 was evaluated. The polarographic (DPP) detection limits for both pesticides, according to the criteria proposed by Winefordner et al. (*12*), are shown in Table II.

The procedures proposed in this work were applied to samples containing different ratios of parathion and paraoxon. Table III shows the results obtained from the determination of parathion by measuring the peak of the *p*-nitrophenol formed at pH* 8.0 and 9.25.

The results obtained at this latter value are more precise due to the better resolution of the *p*-nitrophenol peak (Figure 5).

It is recommended that the determination of paraoxon, when the paraoxon/parathion ratio is less than 1/30, be carried out by the standard addition method (Table IV).

The simultaneous determination of these pesticides is possible with an acceptable margin of error as long as the parathion/paraoxon ratio is greater than 1/45 and that of paraoxon/parathion greater than 1/70. For lower ratios the method is only recommended for the determination of the major species.

Recommended Procedure for the Determination of Mixtures of Parathion and Paraoxon. To a solution containing both pesticides in 30% (v/v) $MeOH/H_2O$ medium with buffer 0.12 M and NaOH, (pH* 8.0) Pd(II) is added at a concentration of 1.0×10^{-4} M. After 120 min, this solution is placed in the polarographic cell, and after removal of the oxygen, the DPP polarogram is recorded. Paraoxon is determined by its reduction peak and parathion by the peak corresponding to the *p*-nitrophenol formed. An alternative method for the indirect measurement of parathion consists of alkalinizing the solution until pH* 9.25, once hydrolysis has taken place, and then measuring the *p*-nitrophenol peak, which under these conditions is better defined. In real samples it is necessary to determine the *p*-nitrophenol present, by measuring its reduction peak, before adding Pd(II).

Registry No. Pd(II), 16065-88-6; parathion, 56-38-2; paraoxon, 311-45-5.

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